



INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁵ : A61L 15/22, 15/58, 15/60 C09J 157/00	A1	(11) International Publication Number: WO 91/09633 (43) International Publication Date: 11 July 1991 (11.07.91)
(21) International Application Number: PCT/US90/07412 (22) International Filing Date: 13 December 1990 (13.12.90) (30) Priority data: 458,246 28 December 1989 (28.12.89) US (71) Applicant: MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, P.O. Box 33427, Saint Paul, MN 55133 (US). (72) Inventor: ASMUS, Robert, A. ; P.O. Box 33427, Saint Paul, MN 55133 (US). (74) Agents: HORNICKEL, John, H. et al.; Minnesota Mining and Manufacturing Company, P.O. Box 33427, Saint Paul, MN 55133 (US).		(81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FI, FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, KR, LU (European patent), NL (European patent), NO, SE (European patent). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: COMPOSITE OF A DISPERSED GEL IN AN ADHESIVE MATRIX AND METHOD FOR PREPARING SAME (57) Abstract A composite of a gel of swollen hydrocolloid dispersed in a pressure sensitive adhesive matrix is provided. The gel has a natural or synthetically derived hydrocolloid swollen with a non-volatile swelling agent, such that the gel may have a shear modulus of less than 6.2×10^6 dynes/cm ² . The gel-adhesive composite has continued skin adhesion whether applied to or existing in dry or moist skin conditions. The gel contributes a high moisture vapor transmission rate to attempt to maintain dry skin conditions while the adhesive maintains skin adhesion. The gel-adhesive composite may be used in a variety of tape, dressing, bandage, drape, or other skin contacting usage and may optionally include antimicrobial agents to treat the skin while adhesion continues.		

Best Available Copy

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AT	Austria	ES	Spain	MG	Madagascar
AU	Australia	FI	Finland	ML	Mali
BB	Barbados	FR	France	MN	Mongolia
BE	Belgium	GA	Gabon	MR	Mauritania
BF	Burkina Faso	GB	United Kingdom	MW	Malawi
BG	Bulgaria	GN	Guinea	NL	Netherlands
BJ	Benin	GR	Greece	NO	Norway
BR	Brazil	HU	Hungary	PL	Poland
CA	Canada	IT	Italy	RO	Romania
CF	Central African Republic	JP	Japan	SD	Sudan
CG	Congo	KP	Democratic People's Republic of Korea	SE	Sweden
CH	Switzerland	KR	Republic of Korea	SN	Senegal
CI	Côte d'Ivoire	LJ	Liechtenstein	SU	Soviet Union
CM	Cameroon	LK	Sri Lanka	TD	Chad
CS	Czechoslovakia	LU	Luxembourg	TG	Togo
DE	Germany	MC	Monaco	US	United States of America
DK	Denmark				

COMPOSITE OF A DISPERSED GEL IN AN ADHESIVE MATRIX
AND METHOD FOR PREPARING SAME

5

Field Of The Invention

The present invention relates to novel
composites of gels of swollen hydrocolloids dispersed in
a pressure sensitive adhesive matrix. The present
invention also relates to the preparation of such
composites, which are useful in medical applications,
such as tapes, dressings, drapes, and antimicrobial
devices.

15

Background Of The Invention

A hydrocolloid is a synthetically prepared or
naturally occurring polymer capable of forming a
thickened gel in the presence of water and polyols.

Hydrogels, hydrocolloids swollen with water or
another hydrophilic liquid have been known for the
purpose of absorbing or retaining moisture or water.
U.S. Patents 4,438,258 and 4,552,138 describe typical
hydrogels.

In medical applications, hydrogels swollen with
water or other liquids generally have good moisture vapor
transmission rates. Hydrogels are quite useful for the
absorbing or removal of body fluids, such as
perspiration, from the pores of the continuous skin of
the patient or from a wound, incision or other opening in
the skin of the patient.

While certain hydrogels can have some pressure
sensitive adhesive properties, the adhesive strength of
hydrogels is marginal for general utility skin adhesives.
Hydrogels alone are generally not used as medical tapes,
dressings, drapes and the like because of lack of good
adhesive strength in either dry skin environments ("dry

35

-2-

stick adhesion") or in moist skin environments ("wet stick adhesion"). Both of these environments require continuous strong adhesion of a tape, dressing, bandage or the like for proper patient care.

5 On the other hand, conventional pressure sensitive adhesives have strong dry stick adhesion, but often lack high moisture vapor transmission properties. For this reason, the adhesion may fail in moist environments occurring beneath medical tapes, dressings, 10 drapes and the like.

 Also, if antimicrobial agents, such as chlorhexidine, are desired to be administered topically to the skin of the patient, these pressure sensitive adhesives alone are poor candidates to provide rapid 15 delivery of the antimicrobial agent to the skin.

 Conventional pressure sensitive adhesives have been mixed with unswollen hydrocolloidal filler material for the purpose of providing wet stick adhesion where initial moist skin environments are common. For example, 20 U.S. Patents 4,166,051 and 4,505,976 describe adhesives with hydrocolloids mixed therein. These mixtures are used as sealants about a skin opening of a patient, such as a stoma, following surgery.

 A stoma sealant requires wet stick adhesion to 25 absorb or wick away moisture or other body fluids from about the skin opening. However, the use of unswollen hydrocolloidal fillers or reinforcers initially make the adhesive much stiffer and less pliable, reducing the dry stick adhesion of the adhesive against the flexible 30 contours of the movable and stretchable skin.

 Furthermore, following the continued absorbance of moisture and other body fluids, inevitably, wet stick adhesion is also reduced. Also such stoma-type adhesives are typically opaque, which, while not important for 35 their usefulness about stomas, limit their usefulness

-3-

where transparent or nearly transparent adhesives are desired in medical applications such as for incise drapes.

Thus, the use of hydrocolloids in the medical applications has progressed in diverging directions. In one direction, swollen hydrocolloids. Hydrogels provide high moisture vapor transmission rates but without significant dry or wet stick adhesive strength. In the other direction, unswollen hydrocolloids mixed into conventional pressure sensitive adhesives to become opaque stoma-type sealants provide wet stick adhesion at the expense of dry stick adhesion.

What is needed in the art is a composite which has the good dry stick adhesion of a strong pressure sensitive adhesive and the high moisture vapor transmission rate of a swollen hydrocolloid. It is desirable to have a composite which has the capability of avoiding loss of adhesion against the skin or skin opening upon continued exposure to moist conditions. It is also desirable to have an adhesive which has translucency approaching transparency and has the ability to release antimicrobial agents in efficacious amounts when placed in contact with the skin.

Summary Of The Invention

The present invention provides a composite of a gel dispersed in an adhesive matrix which continuously transmits moisture vapor while continuously adhered to the skin of a patient. The gel-adhesive composite of the present invention is at least nearly transparent, has a high moisture vapor transmission rate, and has a high peel strength.

The composite is a two phase system of gel and adhesive, where the dispersed phase of the system is a two component gel.

-4-

The gel-adhesive composite requires at least three components: (1) a pressure sensitive adhesive as the continuous matrix; and in the dispersed gel, (2) a hydrocolloid and (3) a swelling agent for the hydrocolloid.

The gel-adhesive composite comprises from about 5 weight percent to about 99 weight percent of a pressure sensitive adhesive composition and from about 1 weight percent to about 95 weight percent of a gel dispersed in the pressure sensitive adhesive composition, the gel comprising a hydrocolloid and a non-volatile hydrocolloid swelling agent having a ratio of weight fractions of hydrocolloid to swelling agent of from about 3:1 to about 1:99.

The pressure sensitive adhesive may be a conventional pressure sensitive adhesive, which is defined by the Pressure Sensitive Tape Council (Glossary of Terms Used in Pressure Sensitive Tape Industry, PSTC, Glenview, Ill. 1959) to be adhesives "which in dry form are aggressively and permanently tacky at room temperature and firmly adhere to a variety of dissimilar surfaces upon mere contact without the need of more than finger or hand pressure." These adhesives "have a sufficiently cohesive holding and elastic nature so that, despite their aggressive tackiness, they can be handled with the fingers and removed from smooth surfaces without leaving a residue." Because pressure sensitive adhesives vary in their strength of adhesiveness, their selection for use in the composite will depend on the final application desired.

The pressure sensitive adhesive is preferably hydrophobic, i.e., tending neither to combine with nor be soluble in water. The natural lack of affinity for water possessed by a hydrophobic pressure sensitive adhesive causes it to separate from and remain immiscible with water or other hydrophilic liquids.

-5-

The swelling agent is a hydrophilic liquid, i.e., tending to combine with and be soluble in water. The natural affinity for water of the swelling agent allows the swelling agent to swell the hydrocolloid, defined above, keeping the swollen hydrocolloid, the gel, separated from and dispersed in the pressure sensitive adhesive.

The difference in hydrophilicity of the swelling agent to the pressure sensitive adhesive sufficient to generate a two phase system, i.e., their incompatibility, is required to maintain sufficient amounts of swelling agent in the hydrocolloidal gel particles dispersed in the pressure sensitive adhesive matrix and to minimize plasticization of the pressure sensitive adhesive, which would cause loss of skin adhesion and increase adhesive residue. Optimally, no amount of swelling agent should migrate into the pressure sensitive adhesive. Preferably, less than 0.5 weight percent of the pressure sensitive adhesive matrix should comprise migrated swelling agent. In no event should more than 5 weight percent of the pressure sensitive matrix comprise migrated swelling agent. In no event should the amount of swelling agent migrated into the pressure adhesive matrix cause the gel to have a ratio of weight fractions of hydrocolloid to swelling agent exceeding about 3:1.

The swelling agent must also be non-volatile, i.e., essentially non-evaporative either at ambient temperatures and pressures or at elevated temperatures used in processing to prepare the gel-adhesive composite. Non-volatile swelling agents allow the gel to remain a gel after processing and during use, preserving the swollen condition of the hydrocolloid for its high moisture vapor transmission properties.

Thus, gel-adhesive composite of the present invention retains the high peel adhesion and high shear adhesion properties of the pressure sensitive adhesive in

-6-

the presence of moisture vapor and other fluids because the high moisture vapor transmission rate property provided by the gel facilitates removal of the moisture or other fluid from the area where the composite is
5 adhered.

The gel-adhesive composite requires at least the pressure sensitive adhesive and the gel of hydrocolloid and swelling agent. Without the pressure sensitive adhesive, the gel may not be strong enough as
10 an adhesive to provide continued adhesion in dry or moist skin conditions. Without the hydrocolloid, no gel can form, and the hydrophilic swelling agent would "bloom" to the surface of the adhesive, thus severely degrading adhesion. Without the swelling agent, the unswollen
15 hydrocolloid in the adhesive may greatly reduce continued dry stick adhesion capability.

The gel-adhesive composite may also include a broad spectrum antimicrobial agent therein to provide medicinal treatment while the composite is adhered to the
20 skin of the patient.

The composite may be coated on a backing material or web also preferably having a high moisture vapor transmission rate to provide strength to the composite and protection from exposure of the skin of the
25 patient to the surrounding environment. The composite resists the loss of adhesion to skin when exposed to moisture, water, exudate, or other fluid present in or about the skin or the skin opening.

13. A method for preparing a composite of a gel dispersed in a pressure sensitive adhesive matrix having a high moisture vapor transmission rate,
30 comprising:

(a) swelling a hydrocolloid with a non-volatile swelling agent to form swollen hydrocolloid gel
35 particles;

-7-

(b) dispersing said gel particles into a hydrophobic solution comprising a pressure sensitive adhesive;

5 One method for preparing a composite of a gel dispersed in a pressure sensitive adhesive matrix comprises swelling a hydrocolloid with a non-volatile swelling agent to form swollen hydrocolloid gel particles, and dispersing said gel particles into a
10 hydrophobic solution comprising a pressure sensitive adhesive, coating said solution on a release liner, and drying said solution to form a continuous pressure sensitive adhesive matrix having said gel particles dispersed therethrough to form a gel-adhesive composite.

15 Alternatively, the gel and the adhesive may be mixed in a latex solution. That method comprises swelling a hydrocolloid with a non-volatile swelling agent compatible with said hydrocolloid to form swollen hydrocolloid gel particles, dispersing said gel particles
20 into a latex mixture comprising a pressure sensitive adhesive, coating said latex mixture on a release liner, and drying said mixture to form a continuous pressure sensitive adhesive matrix having said gel particles dispersed therethrough to form a gel-adhesive composite.

25 Whether prepared using a hydrophobic solution or a latex mixture, any solvents used in preparing the gel and/or the pressure sensitive adhesive are removed, principally by evaporation, to yield the gel-adhesive composite.

30 The gel-adhesive composites of the present invention are achievements of the balancing of two important properties for medical adhesives involving the adhering of a material to the skin or skin opening: (1) significant adhesive strength in dry or moist conditions
35 continuously for an extended period which does not exhaust itself upon initial swelling of hydrocolloidal material, and (2) a high moisture vapor transmission

-8-

rate. The composites of the present invention bridge the gap between high moisture vapor transmission rates provided by hydrogels and significant adhesive strength provided by conventional pressure sensitive adhesives.

5 Consequently, balancing these properties permits the composites of the present invention to provide utility for a wide variety of skin adhesive applications. Nearly transparent composites have great utility as incise drapes, dressings, bandages, tapes of
10 all varieties for use on skin, and other skin contacting uses.

Brief Description Of The Drawing

15 FIG. 1 is a cross-section of a typical coating of the gel-adhesive composite of the present invention on a backing material, showing in the coating the dispersion of the gel throughout the pressure sensitive adhesive matrix.

20 FIG. 2 is a tri-coordinate graph depicting various ranges of weight fractions of pressure sensitive adhesive, hydrocolloid, and swelling agent used to prepare a gel-adhesive composite within the scope of the present invention.

25 Embodiments Of The Invention

THE GEL-ADHESIVE COMPOSITE

30 The gel-adhesive composite of the present invention comprises a two phase system. When used in medical applications, the composite adheres to the surface of the skin of the patient and maintains that surface in as dry an environment as can occur where the skin or skin opening exudes perspiration, or other body fluids.

35

THE PRESSURE SENSITIVE ADHESIVE

In medical application, the pressure sensitive adhesive must be tacky at room temperature as well as at skin temperature of patients. Also, the adhesive must be dermatologically acceptable, i.e., after continuous contact with skin, there is little adhesive residue upon removal and there is no significant reaction with skin during adhesion.

The strength of the pressure sensitive adhesive phase of the composite depends on the type of pressure sensitive adhesive chosen. The adhesives must provide sufficient adhesive strength to adhere the gel-adhesive composite to the skin of the patient.

The pressure sensitive adhesives may be polymeric adhesive compositions prepared from a combination of monomers, homopolymers, copolymers and tackifiers, or blends thereof to produce polymeric adhesive compositions containing polyacrylates, polyolefins, silicone adhesives, natural or synthetically derived rubber base adhesives, or polyvinyl ethers.

Preferably, the pressure sensitive adhesives useful in the composite are hydrophobic allowing the adhesives of the pressure sensitive adhesive to resist absorbing either hydrophilic swelling agent from the dispersed gel or moisture or other body exudate gathering at the skin or skin opening during use. The composite retains its strong adhesiveness even in the presence of water and swelling agents since the pressure sensitive adhesive is unaffected and not plasticized by these agents. Excess moisture is taken away from the skin surface by the gel having a high moisture vapor transmission rate. This prohibits adhesion loss due to pooling of moisture under the adhesive against the skin.

The pressure sensitive adhesive optimally should not absorb any swelling agent and preferably less than 0.5 weight percent of its weight. It has been found that the pressure sensitive adhesive may absorb swelling

-10-

agent in amounts up to 5 weight percent of its weight in certain circumstances without overly plasticizing the pressure sensitive adhesive.

Preferred adhesives are acrylic
5 pressure-sensitive adhesive copolymers comprising "A" and "B" monomers as follows: Monomer A is a hydrophobic monomeric acrylic or methacrylic acid ester of alkyl alcohol, the alkyl alcohol containing 4 to 10 carbon atoms, preferably 6 to 10 carbon atoms, more preferably 6
10 to 8 carbon atoms, and most preferably 8 carbon atoms. Examples of suitable A monomers are n-butyl, n-pentyl, n-hexyl, isoheptyl, n-nonyl, n-decyl, isohexyl, 2-ethyloctyl, isooctyl and 2-ethylhexyl acrylates. The most preferred monomer is isooctyl acrylate.

15 Monomer B is a reinforcing monomer comprising acrylic acid; methacrylic acid; alkyl acrylates and methacrylates containing 1 to 3 carbon atoms in the alkyl group; acrylamide; methacrylamide; lower alkyl-substituted acrylamides (i.e., the alkyl group
20 containing 1 to 4 carbon atoms) such as tertiary-butyl acrylamide; diacetone acrylamide; N-vinyl-2-pyrrolidone; vinyl ethers such as vinyl tertiary-butyl ether; substituted ethylenes such as derivatives of maleic anhydride, dimethyl itaconate and monoethylformate; or
25 vinyl perfluoro-n-butyrate. The preferred B monomers are acrylic acid, acrylamide and N-vinyl-2-pyrrolidone. The most preferred B monomer is N-vinyl-2-pyrrolidone.

The A monomer in such copolymer is present in the pressure sensitive adhesive copolymer in an amount by
30 weight of about 85 to 98 percent by weight, and preferably about 90 to 98 percent by weight of the weight of all monomers in the copolymer.

The B monomer in such a copolymer is present in the pressure sensitive adhesive copolymer in an amount by
35 weight of about 2 to about 15 percent by weight, and preferably about 2 to 10 percent by weight of the weight of all monomers in the copolymer.

-11-

Most preferably, the pressure sensitive adhesive of the present invention is an isooctyl acrylate/N-vinyl pyrrolidone copolymer in a weight fraction ratio of 91:9.

5 The adhesive copolymers of the above type are known and their method of preparation is well known to those skilled in the art, having been described for example, in U.S. Patent RE 24,906 of Ulrich. Since the pressure sensitive adhesives described above are
10 inherently rubbery and tacky and are suitably heat and light stable, there is no need to add tackifiers, crosslinkers, or stabilizers. However, such may be added if desired.

15 The availability and preparation of other pressure sensitive adhesives useful in the present invention are described in the literature. In the Handbook of Pressure Sensitive Adhesive Technology 2nd Ed., Satas, Editor, (Von Nostrand Reinhold, New York 1989), a number of types of useful pressure sensitive
20 adhesives are discussed: natural rubber adhesives; A-B-A block copolymers, (such as polystyrene-polybutadiene-polystyrene (S-B-S), polystyrene-polyisoprene-polystyrene (S-I-S), polystyrene-poly(ethylene/butylene)-polystyrene (S-EB-S),
25 and polystyrene-poly(ethylene/propylene)-polystyrene (S-EP-S) polymers); butyl rubbers and polyisobutylene; vinyl ether polymers; silicones; polyisoprene; butadiene acrylonitrile rubber; polychloroprene; atactic polypropylene; and additional descriptions of acrylic
30 adhesives and acrylic dispersions. Any of these pressure sensitive adhesives may form the polymeric matrix into which the gel may be dispersed.

35 Desirably among these available pressure sensitive adhesives, silicone pressure sensitive adhesives (such as those disclosed in U.S. Patent

-12-

4,039,707) and polystyrene-polyisoprene-polystyrene A-B-A block copolymers (such as those disclosed in U.S. Patent 3,935,338) are useful.

5 THE GEL OF HYDROCOLLOID AND SWELLING AGENT

 The gel of the gel-adhesive composite is hydrophilic to the extent necessary to maintain a dispersion of gel particles in the pressure sensitive adhesive matrix. At the surface of and throughout the composite, the gel particles provide the mechanism to
10 remove the moisture or other body exudate from the skin or skin opening. While the gel may have its own pressure sensitive adhesive properties, it is not necessary. The adhesive matrix provides the necessary adhesiveness which
15 is maintained by the gel's moisture vapor transmission properties.

 The gel in the gel-adhesive composite comprises the hydrocolloid solid and the swelling agent liquid. The ratio of these two constituents of the gel is
20 important to the functioning of the composite. The ratio of the swelling agent to the hydrocolloid and the ratio of the gel to the adhesive provide the basis for balancing the adhesive and moisture vapor transmitting properties of the composite.

25

 THE HYDROCOLLOID

 The hydrocolloid used in the present invention may be any synthetically prepared or naturally occurring polymer capable of forming a thickened gel in the
30 presence of the swelling agent. Varieties of hydrocolloids within the scope of the present invention include synthetic polymers prepared from single or multiple monomers, naturally occurring hydrophilic polymers or chemically modified naturally occurring
35 hydrophilic polymers.

Non-limiting examples of such hydrocolloids include polyhydroxyalkyl acrylates and methacrylates, polyvinyl lactams, polyvinyl alcohols, polyoxyalkylenes, polyacrylamides, polyacrylic acid, polystyrene sulfonates, natural or synthetically modified polysaccharides, alginates, xanthan gums, guar gums, and cellulose.

When used in medical applications, the hydrocolloid must also be dermatologically acceptable and non-reactive with the skin of the patient or other components of the gel-adhesive composite including any antimicrobial agents which may be present in the composite.

Desirably, the hydrocolloid is a synthetic polymer which may be either linear or crosslinked. Non-limiting examples of synthetic hydrocolloids include polymers prepared from N-vinyl lactams, e.g. N-vinyl-2-pyrrolidone, 5-methyl-N-vinyl-2-pyrrolidone, 5-ethyl-N-vinyl-2-pyrrolidone, 3,3-dimethyl-N-vinyl-2-pyrrolidone, 3-methyl-N-vinyl-2-pyrrolidone, 3-ethyl-N-vinyl-2-pyrrolidone, 4-methyl-N-vinyl-2-pyrrolidone, 4-ethyl-N-vinyl-2-pyrrolidone, N-vinyl-2-valerolactam, and N-vinyl-2-caprolactam.

Other monomers useful to prepare a synthetic hydrocolloid include hydroxyalkyl acrylates and methacrylates, (such as 2-hydroxyethyl acrylate, 2-hydroxyethyl methacrylate, 2-hydroxypropyl acrylate, 2-hydroxypropyl methacrylate, 2,3-dihydroxypropyl methacrylate), acrylic acid, methacrylic acid and a tertiary amino-methacrylimide, (e.g. trimethylamino-methacrylimide), crotonic acid, and pyridine.

Other monomers useful to prepare a synthetic hydrocolloid include water soluble amides, (such as N-(hydroxymethyl)acrylamide and -methacrylamide,

N-(3-hydroxypropyl)acrylamide, N-(2-hydroxyethyl) methacrylamide, N-(1,1-dimethyl-3-oxabutyl)acrylamide N-[2-(dimethylamine)ethyl]acrylamide and -methacrylamide, N-[3-(dimethylamino)-2-hydroxylpropyl]methacrylamide, and
5 N-[1,1-dimethyl-2-(hydroxymethyl)-3-oxabutyl]acrylamide); water-soluble hydrazine derivatives, (such as trialkylamine methacrylimide, and dimethyl-(2-hydroxypropyl)amine methacrylimide);
10 mono-olefinic sulfonic acids and their salts, (such as sodium ethylene sulfonate, sodium styrene sulfonate and 2-acrylamideo-2-methylpropanesulfonic acid); and the following monomers containing nitrogen in the non-cyclic or cyclic backbone of the monomer: 1-vinyl-imidazole, 1-vinyl-indole, 2-vinyl imidazole, 4(5)-vinyl-imidazole,
15 2-vinyl-1-methyl-imidazole, 5-vinyl-pyrazoline, 3-methyl-5-isopropenyl-pyrazole, 5-methylene-hydantoin, 3-vinyl-2-oxazolidone, 3-methacrylyl-2-oxazolidone, 3-methacrylyl-5-methyl-2-oxazolidone, 3-vinyl-5-methyl-2-oxazolidone, 2- and 4-vinyl-pyridine,
20 5-vinyl-2-methyl-pyridine, 2-vinyl-pyridine-1-oxide, 3-isopropenyl-pyridine, 2- and 4-vinyl-piperidine, 2- and 4-vinyl-quinoline, 2,4-dimethyl-6-vinyl-s-triazine, and 4-acrylyl-morpholine.

Other hydrocolloidal polymers, either naturally
25 occurring or synthetically prepared, are useful in the present invention. These materials include polyvinyl alcohol, polyoxyalkylenes, and such naturally occurring or synthetically modified hydrocolloidal materials as polysaccharides, gums, and modified cellulose.

30 Representative polysaccharides include starch, glycogen, hemicelluloses, pentosans, gelatin, celluloses, pectin, chitosan, and chitin. Representative gums include Arabic, Locust Bean, Guar, Agar, Carrageenan, Xanthan, Karaya, alginates, tragacanth, Ghatti, and
35 Furcelleran gums. Representative modified celluloses include methyl cellulose, hydroxypropyl methyl cellulose, carboxymethylcellulose, and hydroxypropyl cellulose.

-15-

Crosslinking of the linear polymer chains of the hydrocolloid may be desired to improve cohesive properties of the gel dispersed in the pressure sensitive adhesive matrix. When such crosslinking is desired for polymers made from vinyl monomers discussed above, a multi-ethylenically unsaturated compound with the ethylenic groups being vinyl, allyl, or methallyl groups bonded to nitrogen, oxygen or carbon atoms can be used.

Non-limiting examples of crosslinking agents for vinyl containing polymers include divinyl, diallyl, or dimethallyl esters (e.g. ethylene glycol dimethacrylate, divinyl succinate, divinyl adipate, divinyl maleate, divinyl oxalate, divinyl malonate, divinyl glutarate, diallyl itaconate, diallyl maleate, diallyl fumarate, diallyl diglycolate, diallyl oxalate, diallyl adipate, diallyl succinate, diallyl azelate, diallyl malonate, diallyl glutarate, dimethallyl maleate, dimethallyl oxalate, dimethallyl malonate, dimethallyl succinate, dimethallyl glutarate, and dimethallyl adipate); divinyl, diallyl or dimethallyl ethers (e.g. diethyleneglycol divinyl ether, butane diol divinyl ether, ethylene glycol divinyl ether, ethylene glycol diallyl ether, diethylene glycol diallyl ether, butane diol diallyl ether, ethylene glycol dimethallyl ether, diethylene glycol dimethallyl ether, and butane diol dimethallyl ether); divinyl, diallyl or dimethallyl amides including bis(N-vinyl lactams), (e.g., 3,3'-ethylene bis(N-vinyl-2-pyrrolidone) and methylene-bis-acrylamide); and divinyl, diallyl and dimethallyl ureas.

Preferable crosslinking agents include ethylene glycol dimethacrylate, methylene-bis-acrylamide, diallyl maleate, and 3,3'-ethyldiene bis (N-vinyl-2-pyrrolidone).

For n-vinyl lactams, the preferred crosslinking agents are diallyl maleate and 3,3'-ethyldiene bis (N-vinyl-2-pyrrolidone).

-16-

For acrylates and methacrylates, the preferred crosslinking agents are ethylene glycol dimethacrylate and methylene-bis-acrylamide.

Preferred hydrocolloids for the present invention are linear or crosslinked polyvinyl lactams. Of the polyvinyl lactams, N-vinyl-2-pyrrolidone is preferred.

When crosslinking is desired, such crosslinking agents as diallyl maleate or 3,3'-ethylidene bis (N-vinyl-2-pyrrolidone) may be used to crosslink such polyvinyl lactams generally and poly-N-vinylpyrrolidone particularly.

Preferably, the crosslinked hydrocolloid is poly-N-vinylpyrrolidone prepared from the reaction of from about 97 to about 99.92 percent by weight of N-vinyl-2-pyrrolidone and from about .08 to about 3 percent by weight of 3,3'-ethylene bis N-vinyl-2-pyrrolidone. Most preferably, the 3,3'-ethylene bis N-vinyl-2-pyrrolidone comprises about 0.16 percent by weight of the poly-N-vinylpyrrolidone.

THE SWELLING AGENT

The swelling agent for the hydrocolloid may be a broad variety of liquids which are non-volatile or non-evaporative in ambient climatic conditions, and which are also incompatible with or extremely insoluble in the pressure sensitive adhesive or its solvent(s). The swelling agent must also be capable of swelling the hydrocolloid chosen, in order to form the gel phase of the composite of the present invention.

Non-volatility avoids evaporative loss of the swelling agent from the gel, thereby retaining the gel's moisture vapor transmission utility for continued periods. Non-volatility for the swelling agent is desired not only at room or body temperatures but also at the elevated temperatures of processing which range from about 75°C to about 250°C. Because these non-volatile

-17-

swelling agents have humectant properties at room temperatures, it is better to characterize an acceptable minimum amount of non-volatility at elevated temperature. For example, acceptable swelling agents for the present invention are sufficiently non-volatile if less than 10 percent of a given volume evaporates after exposure to a temperature of 75°C for one hour.

Incompatibility avoids plasticization of the pressure sensitive adhesive by the swelling agent. No significant migration of the swelling agent into the pressure sensitive adhesive occurs because of their relative mutual insolubility. When the swelling agent is hydrophilic and the pressure sensitive adhesive preferably is hydrophobic, there is a continuous and strong tendency for phase separation.

Because the swelling agent is incompatible with the pressure sensitive adhesive, there is no significant migration of the swelling agent liquid from the gel phase into the adhesive matrix. A swelling agent compatible with the pressure sensitive adhesive would undesirably plasticize the adhesive, destroying its effectiveness as a skin adhesive.

Optimally, no swelling agent should migrate from the gel to the pressure sensitive adhesive matrix. Plasticization of the pressure sensitive adhesive is avoided if less than about 5 weight percent of swelling agent migrates into the pressure sensitive adhesive matrix. However, in no event should the weight fraction ratio of hydrocolloid to swelling agent exceed 3:1. Thus, depending on the weight fraction ratio of pressure sensitive adhesive to gel, up to about 5 weight percent of swelling agent can migrate into the pressure sensitive adhesive without harming the properties of the gel or the adhesive of the composite. But less than 2 weight percent is acceptable in most instances, with less than than 1 weight percent being desirable and less than 0.5 weight percent being preferred.

Varieties of non-volatile swelling agents within the scope of invention, which are incompatible with the pressure sensitive adhesives contemplated herein, include room temperature liquid polyols, (including polyhydric alcohols), such as glycerol, propylene glycol, poly(ethylene) glycol (having a molecular weight in the range of about 200 to about 600) and polypropylene glycol (having a molecular weight in the range of about 350 to about 1,000); room temperature solid polyols (including polyhydric alcohols), (such as sorbitol, erythritol, threitol, ribitol, arabinitol, xylitol, allitol, talitol, mannitol, glucitol, glactitol, iditol, pentaerythritol, heptitol, octitol, nonitol, decitol, and dodecitol), blended with a room temperature liquid polyol; monoanhydroalditols (such as styrcitol, polyalitol, D-Fructose, 1,4 anhydro D-mannitol and 1,4 anhydro-D-glucitol) blended with a room temperature liquid polyol; monosaccharides (such as pentoses, hexoses, and heptoses) blended with a room temperature liquid polyol; and ether alcohols, such as poly(ethylene) glycol ether (having a molecular weight in the range of 600 to 20,000) and polypropylene glycol ether (having a molecular weight in the range of 1,000 to 5,000) blended with a room temperature liquid polyol.

Of these polyols, desirable swelling agents are glycerol, propylene glycol, polyethylene glycol (200-600 molecular weight) and sorbitol blended with glycerol. Because of its non-volatility and low-cost availability, glycerol is the preferred swelling agent.

Optionally, volatile solvents such as water and monohydric alcohols may be used to assist in the preparation of the gel by initiating the swelling of the hydrocolloids or in aiding the dispersion of the gel particles in a hydrophobic pressure sensitive adhesive matrix. Whether in a hydrophobic solution or in a suspension or emulsion, such processing volatile agents are not considered swelling agents of the present

invention. The extent of removal of these volatile solvents is dependant on the requirements of the product application. In addition, depending on the air tightness of the packaging of a product incorporating a composite of the present invention, the gel particles therein may absorb atmospheric moisture. This may also be more or less desirable again depending on the product application.

10 INTERRELATED WEIGHT FRACTIONS OF GEL AND
ADHESIVE AND WEIGHT FRACTION RATIO OF HYDROCOLLOID TO
SWELLING AGENT

To achieve a balance of pressure sensitive adhesive properties and gel properties, the weight fractions of gel and adhesive in the resulting composite are controlled. However, because of the broad scope of properties which may be balanced, the gel may be dispersed in an amount by weight of about 1 to 95 percent by weight of the combined weight of gel and adhesive in the composite.

20 To achieve the proper gel properties in view of the weight fractions of the gel and the adhesive, the weight fractions of the hydrocolloid and the swelling agent are controlled using weight fraction ratios for them.

25 The pressure sensitive adhesive may have a weight fraction of from about 5 to about 99 percent by weight of the gel-adhesive composite. Desirably, the weight fraction of the adhesive in the gel-adhesive composite ranges from about 20 to about 95 percent by weight. Preferably, the weight fraction of the pressure sensitive adhesive in the gel-adhesive composite is from about 25 to about 90 parts by weight.

30 The hydrocolloid may have a weight fraction of from about 0.01 percent to about 72 percent of the gel-adhesive composite of the present invention. Desirably, the weight fraction of the hydrocolloid in the

gel-adhesive composite ranges from about 0.05 to about 48 percent. Preferably, the weight fraction of the hydrocolloid in the gel-adhesive composite ranges from about 0.50 to about 30 weight percent.

5 The swelling agent may have a weight fraction of from about 0.25 to about 95 percent by weight of the gel-adhesive composite. Desirably, the range of the weight fraction of the swelling agent in the composite depends on the weight fraction of the hydrocolloid in the
10 composite.

 Depending on the properties desired for the gel-adhesive composite, the range of weight fraction ratios for the hydrocolloid to the swelling agent can be from about 3:1 to about 1:99. At the ratio of about 3:1,
15 there is sufficient swelling agent to achieve a soft and pliable gel suitable for maintaining the strong adhesiveness of the composite. At the ratio of about 1:99, there is sufficient hydrocolloid to prevent the swelling agent from migrating through the pressure
20 sensitive adhesive and "blooming" to the surface of the composition, thereby destroying its adhesiveness.

 Desirably, the ratio of weight fractions of the hydrocolloid to the swelling agent is from about 1.5:1 to about 1:19. Preferably, based on a balancing of the
25 performance of the moisture vapor transmission rate of the gel with the adhesiveness of the adhesive in the composite, the ratio of the weight fractions of the hydrocolloid to the swelling agent is from about 1:1.5 to about 1:19.

30 FIG. 2, a tri-coordinate graph, provides a convenient depiction of the acceptable, desirable and preferable weight fraction ratios of the three necessary components of the gel-adhesive composite of the present invention. FIG. 2 also depicts the ranges of
35 acceptable, desirable and preferable weight fraction ratios of the hydrocolloid and the swelling agent within the gel of the present invention.

The area in FIG. 2 inside lines A, A¹, and A² graphically depicts that the weight fraction of the pressure sensitive adhesive is from about 5 to about 99 percent, the weight fraction of the hydrocolloid is from about 0.01 to about 72 percent, and the weight fraction of the swelling agent is from about 0.25 to about 94 percent as adjusted for the ratios of the hydrocolloid to the swelling agent of from about 3:1 to about 1:99 (the slopes of the lines A and A², respectively).

For example, a composite containing 20 percent by weight of the pressure sensitive adhesive, 60 percent by weight of the hydrocolloid, and 20 percent by weight of the swelling agent appears on line A and hence at the border of the acceptable area, where the ratio of the hydrocolloid to the swelling agent is 3:1. For example, a composite having 50 percent by weight of the pressure sensitive adhesive, about 1 percent by weight of the hydrocolloid, and about 49 percent by weight of the swelling agent is on line A² within the acceptable area, where the ratio of the hydrocolloid to the swelling agent is about 1:99.

A weight fraction of 60 percent for the pressure sensitive adhesive, 20 percent by weight of the hydrocolloid, and 20 percent by weight of the swelling agent yields a composite clearly within the area in FIG. 2 bounded by lines A, A¹, A² where the ratio of the hydrocolloid to the swelling agent is 1:1.

The areas bounded by bordering lines B, B¹, B² and B³ and C, C¹, C² and C³ in FIG. 2 similarly identify the desirable and preferable weight fractions of the composites of the present invention, respectively. The example in the prior paragraph of the weight percent pressure sensitive adhesive:hydrocolloid:swelling agent ratio of 60:20:20 is also within the desired range of weight fractions bounded by lines B-B¹-B²-B³, where the desired ratio of hydrocolloid to swelling agent of 1:1. But an adhesive:hydrocolloid:swelling agent ratio of

50:10:40 is only within the preferred area of weight percent ranges, bounded by lines C-C¹-C²-C³, where the ratio of hydrocolloid to swelling agent is 1:4.

The bordering lines also demonstrate the desired and preferred hydrocolloid:swelling agent ratios. Line B¹ has a slope matching the hydrocolloid:swelling agent ratio of 1.5:1. Line B³ has a slope matching the ratio of 1:19. Line C¹ has a slope matching the ratio of 1:1.5. Shorter Line C³ has the same slope as the slope of longer Line B³, 1:19.

As stated previously, optimally no swelling agent in the gel should migrate into the adhesive matrix. Preferably less than 0.5 weight percent, and desirably less than 1 weight percent, of the adhesive matrix should comprise migrated swelling agent.

In no event should the amount of swelling agent remaining in the gel cause the hydrocolloid:swelling agent ratio to exceed about 3:1.

Further, in no event should the amount of swelling agent migrating into the adhesive matrix exceed 5 weight percent of the adhesive. This avoids plasticization of the adhesive and reduction of adhesive strength. Residuing of adhesive on the skin is also avoided.

The above constraints define the outer limits of tolerance of swelling agent migration. It is desirable to select swelling agents and pressure sensitive adhesives which are incompatible, to avoid reaching such outer limits. Such incompatibility of swelling agent and adhesive preserves the softness and moisture vapor transmission rate properties of the gel particles dispersed within the adhesive matrix for composites of all ratios of the present invention.

OPTIONAL COMPONENTS

The addition of a variety of biologically active materials into the gel-adhesive composite of the

present invention is desirable when the composite is placed in contact with the skin or skin opening of a patient. Bandages, tapes, dressings, drapes, and the like are all used in conditions where it is desirable to
5 reduce bacteria levels to minimize infection risk or to treat the effects of infections at the skin or skin openings of a patient. For example, in the application of composites of the present invention as incise drapes, antimicrobial agents may be incorporated into the gel of
10 the composition. Broad spectrum antimicrobial agents are disclosed in U.S. Patent No. 4,310,509.

Useful antimicrobial agents include a wide variety of agents which are compatible with both the gel and the pressure sensitive adhesive of the composite.
15 These agents can be incorporated prior to polymerization or gelation of the hydrocolloid, provided they do not interfere with such reaction(s). Alternatively, the agents can be incorporated after polymerization of the hydrocolloid, if any. In the latter case, the
20 antimicrobial agents are dissolved or dispersed in either non-volatile swelling agent or volatile solvent.

Examples of antimicrobial agents are numerous, but desirably such antimicrobial agents as
25 parachlorometaxyleneol; chlorhexidine and its salts such as chlorhexidine acetate and chlorhexidine gluconate; iodine; iodophors; poly-N-vinylpyrrolidone-iodophors; silver oxide, and silver and its salts, and antibiotics (e.g., neomycin, bacitracin, and polymyxin B) are useful in accordance with the present invention.

30 The antimicrobial agents may be included in the composites in a weight from about 0.01 percent to about 10 percent by weight of the total composite after the weight percents of the adhesive, hydrocolloid and swelling agent are determined.

35 Other additives may be incorporated into the composite to enhance the physical properties of the adhesive and the antimicrobial properties of the

composite containing an antimicrobial agent. For example, iodates and iodides may be added to enhance the solubility of the iodine antimicrobial agent during the introduction of the antimicrobial agent into the gel and to adjust the free iodine in the composite.

Photoinitiators, and other catalysts may be used in the polymerization processes for the pressure sensitive adhesive and in the polymerization or gelation of the hydrocolloid.

Compounds to buffer the pH of the composite may be added to provide a non-irritating pH for use with sensitive skin tissue or to otherwise maximize antimicrobial activity.

Further, the incorporation of a surfactant into the composite may improve antimicrobial activity in or at the skin of the patient.

PREPARATION OF THE GEL-ADHESIVE COMPOSITE

There are two methods currently known for the preparation of the composite of the present invention. Both methods involve the separate preparation of the pressure sensitive adhesive and the gel following by the mixing and drying of them to form the composite.

One method involves mixing the gel either with or without a hydrophilic solvent into an adhesive in bulk or in a volatile solvent. The other method involves mixing the gel into a latex adhesive with volatile hydrophilic solvent or solvents.

When the method used involves gel particles mixed into an adhesive in bulk or in a volatile, hydrophobic solvent, the gel particles must be dispersed into the adhesive. Equipment such as a "Laboratory Dispersator, Series 2000, Model 84" mixer, commercially available from Premier Mill Corporation of Reading, Pennsylvania may be used for solution preparation. A Banbury mixer could be used for bulk preparation. The process of mixing should continue until the gel particles

are fully dispersed in the adhesive. Then, the mixing is stopped to allow for the removal of any bubbles created during the mixing process. The mixing process may occur at ambient temperatures and pressures.

5 When the composite is prepared by mixing the gel particles into a latex solution of the hydrophobic pressure sensitive adhesive, the mixing may be accomplished by using the "Laboratory Dispersator" mixer described above. The mixing process may occur at ambient
10 temperatures and pressures. The mixing should continue until the gel particles are fully dispersed. Then the mixing is stopped to allow for the removal of any bubbles created during the mixing process.

 Regardless of the method of preparation,
15 whenever a volatile solvent for the pressure sensitive adhesive, the gel, or both is present during the final mixing, it/they must be removed, generally by application of heat or other drying mechanism. As drying occurs, the adhesive forms a nearly continuous matrix with the gel
20 particles dispersed therein. The temperatures of evaporating the volatile solvent(s) without adversely affecting the remaining adhesive and gel depends upon the type of volatile solvent(s) employed. Generally, however, the mixture is dried at temperatures between
25 about 75°C and about 250°C.

 The resulting composite may be spread or coated onto a release liner and dried to form films having thicknesses of from about 10 to about 1,000 microns and desirably from about 20 to about 100 microns.
30 Thereafter, depending on the desired application, the layer of composite may be applied to a backing material by laminating.

 In elevated temperature preparations, the composite can endure temperatures in excess of 100°C
35 without chemical or physical deterioration. If a biologically active material such as an antimicrobial

agent is included in the composite, the temperature of the drying of the composite and its lamination to a backing material should not exceed 100°C.

5 PREPARATION OF THE PRESSURE SENSITIVE ADHESIVE

 The preparation of the pressure sensitive adhesive depends on the type of adhesive, the type of polymerization (e.g., addition or condensation), and the polymerization technique (e.g., bulk, solution, suspension or emulsion polymerization).

10 The pressure sensitive adhesive polymerization technique chosen is selected from conventional polymerization technique(s) known for a particular pressure sensitive adhesive. Sources of polymerization preparation techniques include Organic Polymer Chemistry, 15 K.J. Saunders, Chapman and Hall (Halsted Publishing, New York, 1973), Applied Polymer Science, R. W. Tess and G. W. Poehlein, American Chemical Society (American Chemical Society, Washington, D.C., 1981), and Principles of Polymerization, 20 George Odien, Wiley-Interscience (John Wiley and Sons, New York, 1981), and the Handbook of Pressure Sensitive Adhesive Technology, 2nd Ed., supra.

 For example, acrylic pressure sensitive adhesives may be prepared according to U.S. Patent RE 25 24,906. When prepared by solution polymerization, the monomers are soluble in solvents, commonly ethyl acetate, cyclohexane, toluene, and n-heptane. The polymer is also usually soluble in the solvent allowing a pure polymer to be coated onto a surface and then dried. When prepared 30 by emulsion polymerization, the latex of water-insoluble polymers in water maintains a phase separation until removal of the water.

 Pressure sensitive adhesives may be prepared by solution polymerization from A-B-A block copolymers, 35 natural rubber, styrene-butadiene, polyisoprene, butyl rubber, polyisobutylene, polychloroprene, and blends

thereof. Pellets of the commercially available polymer are mixed into a solvent and heated in the presence of tackifiers and often plasticizers, in order to develop a non-rigid polymer having the requisite tack. Chapters 11, 13, 14, and 19 of the Handbook of Pressure Sensitive Adhesive Technology 2nd Ed., referenced above, discusses the choices of materials and methods of preparation. A frequently used tackifier is polyterpene resin.

The rubber based adhesives may also be prepared in a latex. For example, styrene and butadiene may be dispersed in water with an emulsifier (such as sodium alkyl benzene sulfonate) and an initiator (such as potassium persulfate). Polymerization occurs typically anaerobically with mixing for about 16-24 hours at 60°C. Chapter 12 of the Handbook of Pressure Sensitive Adhesive Technology 2nd Ed., supra, describes such latex preparation processes.

Silicone pressure sensitive adhesives are usually commercially supplied in a hydrocarbon solvent. Upon evaporation, the silicones exhibit pressure sensitive adhesive properties. As described in Chapter 18 of the Handbook of Pressure Sensitive Adhesive Technology 2nd Ed., supra, a catalyst (such as an organic peroxide, an amino silane, or a metal salt of an organic acid) is added to reinforce the silicone network, increasing cohesiveness.

The polymerization of vinyl ether homopolymers may be carried out by batch processing, or continuous processing in bulk or in solution. Whichever processing is used, cationic initiators such as BF_3 or AlCl_3 are present. Copolymers of vinyl ethers and acrylates are polymerized by free radical emulsion polymerization in water with potassium peroxodisulfate. Chapter 17 of the Handbook of Pressure Sensitive Adhesive Technology 2nd Ed., supra, describes the polymerization.

If volatile solvents are necessary or desirable for the preparation of the pressure sensitive adhesive, such solvents should be hydrophobic and generate phase separating regions when encountering the gel particles having hydrophilic swelling agents therein or volatile hydrophilic solvents used to prepared the gel. Desirably, hydrophobic volatile solvents for the pressure sensitive adhesive are aliphatic or aromatic hydrocarbons, such as heptane, toluene, xylene, and the like and blends containing other miscible solvents such as ethyl acetate.

PREPARATION OF THE GEL

The preparation of the gel involves the mixing or swelling of finely divided particles of the hydrocolloid with the swelling agent and optionally a volatile solvent or solvents compatible or miscible with the swelling agent but incompatible with the adhesive.

The preparation of the gel occurs after preparation of the hydrocolloid and its separation into finely divided particles. A swelling agent is then added in amounts sufficient to achieve the desired weight fraction ratio. The swelling agent swells the hydrocolloid prior to any mixing with the adhesive, such that the swollen gel particles are fully formed prior to being dispersed in the pressure sensitive adhesive matrix.

Swelling may occur at ambient or elevated temperatures (up to 100°C) and ambient pressures in a mixing vessel with simple hand mixing or stirring. The swelling may occur in the presence of such volatile, hydrophilic solvents as water, ethanol, methanol and other monohydric alcohols. However, to the extent possible, it is desirable to swell the hydrocolloid without volatile solvents to avoid the subsequent efforts to remove the solvent to form the composite.

PREPARATION OF THE HYDROCOLLOID

The preparation of the hydrocolloid depends on the choice of hydrocolloid used. If the hydrocolloid is naturally occurring then it is used directly. If the hydrocolloid is synthetic or synthetically modified from a naturally occurring material, the synthesis may be by a variety of methods including condensation polymerization or addition polymerization from monomeric units. The choice of hydrocolloid polymerization technique may be selected based on the hydrocolloid in reference to conventional polymerization technique(s) known for that hydrocolloid. Sources of polymerization preparation techniques include Organic Polymer Chemistry, K.J. Saunders, Chapman and Hall, Applied Polymer Science, R. W. Tess and G. W. Poehlein, American Chemical Society, and Principles of Polymerization, George Odien, Wiley-Interscience, supra.

Desirably, a free radically polymerized hydrocolloid is prepared by photochemically activated polymerization. The monomer, desirably also a crosslinking agent, and the photoinitiator can be polymerized in bulk or in a hydrophilic solution of the swelling agent alone or with other hydrophilic solvents which may be volatile. The precursor can be coated on a flat surface and irradiated with ultra-violet light. Optionally, the hydrocolloid can be ground into particles, emulsified in a volatile solvent and reprecipitated to remove any unreacted monomer, and then dried and ground into a fine powder.

Photoinitiators available for use are well known and have been described in the polymerization art, e.g., Chapter II of "Photochemistry" by Calvert and Pitts, John Wiley and Sons (1966) and in Progress in Organic Coatings, 13 (1985) 123-150. Representative examples of such initiators include acyloins and related compounds such benzoin, benzoin methyl ether, benzoin ethyl ether, benzoin isopropyl ether, benzoin isobutyl

ether, alpha-methylbenzoin, and
2-hydroxy-2-methyl-1-phenyl-1-propanone; and benzilketals
such as benzildimethylketal and benzildiethylketal. A
presently preferred photoinitiator is
5 2-hydroxy-2-methyl-1-phenyl-1-propanone.

Generally, the photoinitiator is used in
amounts ranging from about 0.01 to about 5 percent by
weight of monomer. Preferably, about 0.02 to 2 percent
by weight of photoinitiator is used. When the activating
10 energy is ultraviolet light, the irradiation is typically
initiated at a temperature in the range of 0°C to 50°C
for 0.5 minutes to 5 hours or more depending upon the
intensity of the radiation.

When poly N-vinylpyrrolidone is the
15 hydrocolloid chosen, polymerization may take place in
solution, bulk, or suspension. When
N-vinyl-2-pyrrolidone is polymerized in a hydrophilic
solution of a solvent and/or the swelling agent, the
solids achieved are swollen gel particles which may be
20 ground into fine particles. Desirably, the swelling
agent may serve as the solvent.

When the polymerization of
N-vinyl-2-pyrrolidone is in bulk, a hard polymer is
obtained which must also be ground into fine particles
25 prior to swelling such particles with the swelling agent.

However obtained, the hydrocolloid particles
are swollen with the swelling agent to yield soft and
pliable gel particles. As described above, the swollen
gel particles are dispersed into the adhesive solution
30 using a high shear grinder or mixer to physically
randomly disperse the gel particles of various dimensions
into the pressure sensitive adhesive matrix.

USEFULNESS OF THE GEL-ADHESIVE COMPOSITE

35 Referring to FIG. 1, the usefulness of the
composite may be seen. The gel-adhesive layer 10
comprises a plurality of discrete gel particles 30

dispersed in the continuous matrix of the pressure sensitive adhesive 20. The layer 10 is contacting both a layer 40 of backing material and a release liner 50.

5 The discrete gel particles 30 are of various sizes and are dispersed randomly in the adhesive 20. The variety of sizes depends on the size of the hydrocolloid particle prior to swelling and gel break-up during dispersive mixing or shearing. Desirably, the particles 30 range from about 1 micron to about 600 microns.

10 The composite of the present invention may be coated onto a variety of webs or backing materials 40, including films, substrates, or other elastic, porous or breathable woven or nonwoven materials useful in medical applications. A release liner 50, typically a silicone
15 release liner, protects the other exposed surface of the coated layer 10.

In such manner, the release liner 50 is removed and the layer 10 of composite may be applied to the skin of the patient as a part of a medical tape, a surgical
20 drape, an incise drape, a wound dressing, a bandage of general medicinal utility, or other medical device. The adhesiveness of the pressure sensitive adhesive combined and balanced with the high moisture vapor transmission rate properties of the gel permits wide utility in
25 medical applications.

The composite layer 10 may be coated on a layer 40 of any of several backing materials also having a high moisture vapor transmission rate for use as medical tapes, dressings, drapes, bandages, and the like.
30 Suitable backing materials include those disclosed in U.S. Patents 3,645,835 and 4,595,001. Other examples of a variety of films commercially available as extrudable polymers include "Hytrel^R 4056" and "Hytrel^R 3548" branded polyester elastomers available from E.I. DuPont
35 de Nemours and Company of Wilmington, Delaware, "Estane"

branded polyurethanes available from B.F. Goodrich of Cleveland, Ohio or "Q-thane" branded polyurethanes available from K.J. Quinn & Co. of Malden, Massachusetts.

5 The layer 10 combined with a layer 40 of suitable backing material may be used as a surgical drape, and particularly an incise drape. Suitable backing materials are disclosed in U.S. Patents 4,627,427 or 3,809,077, to be used for incise drapes or surgical drapes, respectively.

10 When used as an incise drape, the composite may be used with a film prepared from "Hytrel 4056" branded polyester elastomer available from DuPont as the backing material.

15 The composite layer 10 can be coated on the backing layer 40 by a variety of processes, including, direct coating, lamination, and hot lamination. The backing layer 40 may also be a release liner onto which the composite is coated prior to drying.

20 The method of applying the composite to the release liner involves the same coating process as that described above for the preparation of the composite after the drying step. The methods of lamination and hot lamination involve the application of pressure, or heat and pressure, respectively, on the layer of composite
25 layer 10 to the backing material layer 40. The temperature for hot lamination ranges from about 50°C to about 250°C, and the pressures applied to both lamination and hot lamination range from 0.1 Kg/cm² to about 50 Kg/cm².

30 The balance of adhesive and moisture vapor transmission properties desired can depend on the climatic conditions where the composite may be used. Diaphoretic patients or patients in intemperate climates where perspiration is unwanted but constantly present may
35 use composites which emphasize high moisture vapor transmission rates over the adhesiveness of the tape, bandage, or dressing used. Conversely, in temperate

climates or even in the chilled conditions of modern operating rooms, the composites which emphasize strong adhesives for use as incise drapes and which have near transparency and continuously good moisture vapor transmission of body fluids are needed.

High moisture vapor transmission rates of the composite encourage a rate of moisture withdrawal from the surface of the skin which thereby attempts to maintain dry skin conditions under the tape, dressing, drape and the like. The adhesive matrix thus remains adhered. In addition to maintaining continued good adhesion, low skin or wound moisture levels reduce the risk of infection.

As described above, optionally, the composite may contain an antimicrobial agent in gel-adhesive layer 10 help reduce infection at the skin or skin opening.

While FIG. 1 and various examples appearing below have described the use of the composite with a backing web or substrate, the scope of the invention is not so limited. There are circumstances where a backing layer would not be desired and the adhesive would be used as a coating alone on the skin or skin opening. Examples of uses of the coating alone include the use of the composite to hold two pieces of skin tissue together or the composite to hold a liquid absorbing material, such as gauze, in contact with the skin.

While the composites of the present invention have particular utility in the medical or veterinary applications, the utility of the composites is not so limited. A wide variety of adhesive composites having continuous moisture vapor transmission capability may be used for application to inanimate objects which must be kept dry notwithstanding a continuing exuding of moisture or water. The securement of a tape to repair torn material exposed to wet environments, such as a tent, may be aided by the use of the composite of the present

invention because the moisture vapor transmission rate of the tape will attempt to provide continued dry stick adhesion.

5 PROPERTIES OF THE GEL-ADHESIVE COMPOSITE

Referring again to FIG. 1, the gel particles 30 dispersed in the continuous adhesive matrix 20 provide the means by which moisture at the skin is continuously removed by diffusion of moisture through the gel-adhesive layer 10.

While not being bound to any particular theory, it is believed that the swelling of the hydrocolloid with the non-volatile swelling agent at weight fraction ratios from 3:1 to 1:99 prior to mixing of the gel with the adhesive provides a high diffusion rate environment for moisture and antimicrobial to rapidly diffuse through the gel. By comparison, the hard, unswollen hydrocolloid particles in stoma-type adhesives have very low diffusion rates and require swelling of the hydrocolloid by moisture prior to providing high moisture or antimicrobial agent diffusion through that type of adhesive.

Thus, the gel particles 30 more quickly and more efficiently transport the moisture from the skin because the gel particles 30 are already in a swollen equilibrium before any contact with the wet or moist environment of the skin. Because the swelling agent is non-volatile, the equilibrium is maintained both before the composite is used and during use in contact with skin. The volatile moisture is transmitted, not the non-volatile swelling agent. These particles 30 attempt to continuously dry an otherwise wet environment by the transmission of moisture from the skin or the skin opening while the adhesive matrix 20 maintains adhesion.

In addition to the interrelated weight fractions of the pressure sensitive adhesive, the hydrocolloid, and the swelling agent and the ratio of the

hydrocolloid to the swelling agent, it is important for the present invention to have gel particles 30 in the composite 10 which are very soft and pliable. If the particles 30 are not soft and pliable, the particles
5 begin to become reinforcing materials in the adhesive matrix 20, stiffening the gel-adhesive composite layer 10 and diminishing the composition's adhesiveness.

The soft and pliable gel particles 30 permit the adhesive matrix 20 of the gel-adhesive composite
10 layer 10 to continue to adhere to the skin in those regions where the gel particles 30 do not contact the skin.

Shear modulus is a measurement of the softness and pliability desired for the gel of the present
15 invention. Generally the shear modulus of the gel particles 30 should be less than 6.2×10^6 dynes/cm².

A desirable upper limit for the shear modulus of the gel of the present invention is 1.5×10^5 dynes/cm². A more preferred maximum of shear modulus for
20 the gels of the composites of the present invention is 4.2×10^4 dynes/cm².

As is known to those skilled in the art, the shear modulus upper limit of 6.2×10^6 dynes/cm² represents an extremely soft material compared with other
25 elastomers known to those skilled in the art.

The balance of the high moisture vapor transmission rate and the continued adhesive properties for that composite are also influenced by the particle size of the gel particles 30 in the adhesive matrix 20.
30 It is axiomatic that smaller particles offer a larger surface area to volume ratio, which helps increase moisture vapor transmission. But it has also been noted that particle sizes for the gel which approximate the thickness of layer gel-adhesive composite 10 of the
35 composite are believed to act as a pore in the matrix of the adhesive, thereby also increasing the moisture vapor transmission rate.

Thus, a wide range of particle sizes may yield acceptable gel-adhesive composite results. A range of particle size for the gel particles 30 of from about 1 to about 600 microns is acceptable, while a range of particle size of from about 25 to about 100 microns is desirable.

The gel particles 30, soft, in swollen equilibrium and of various sizes dispersed in the adhesive matrix 20, can provide to the layer 10 a significantly higher moisture vapor transmission rate than the same adhesive without a gel dispersed therein. The amount of increase depends on the amount of gel dispersed in the adhesive matrix and the size of the gel particles so dispersed. One may increase the moisture vapor transmission rate property of an adhesive by dispersing gel particles therein. Also, one may improve adhesion with a thicker adhesive layer in a medical article while maintaining the moisture vapor transmission rate property of the original thickness of adhesive by dispersing gel into the thicker adhesive matrix. Thus, the moisture vapor transmission rate properties of a gel-adhesive composite of the present invention can be tailored to the use for the composite.

For example, it has been found with acrylate adhesives having as little as 10 weight percent of poly(N-vinyl lactam) particles swollen with glycerol, displays a 20 percent increase in the moisture vapor transmission rate. When there are substantial weight fractions of gel in the composite, for example, between 50 and 75 weight percent, the moisture vapor transmission rates can be as much as 200 to 700 percent greater than the pressure sensitive adhesive displays.

The high moisture vapor transmission rates achieved by the gel of the composite do not adversely impact the adhesion strength of the pressure sensitive adhesive. Initially, short term (a few hours), and long term (24 hours) adhesion values of the gel-adhesive

composites having a broad range of gel concentrations follow the adhesion values of the pressure sensitive adhesive over the same periods. For example, in a preferred embodiment of poly (N-vinylpyrrolidone) hydrocolloid in glycerol swelling agent, the gel comprising 25 percent by weight of the composite, where the ratio of hydrocolloid to swelling agent was 1:1, the skin adhesion of the composite after 24 hours was nearly as great as the skin adhesion for the pressure sensitive adhesive alone after 24 hours.

Further, the gel-adhesive composites display excellent wet adhesion properties making the composite equally attractive to patient care conditions where dry skin environments become wet or where wet skin environments must be made drier.

The peel adhesive strength of the composites of the present invention are strong notwithstanding the presence or absence of humidity. For example, in a composite having about 75 percent by weight of an acrylate pressure sensitive adhesive and about 25 percent by weight of poly (N-vinyl lactam) gel, within which the lactam hydrocolloid to glycerol swelling agent ratio was about 0.43:1, the T-Peel adherence to low density polyethylene (LDPE) (which is used to simulate skin adhesion) at dry or humid conditions was better than the adhesiveness of the acrylate pressure sensitive adhesive alone. The humid LDPE test at 50 percent relative humidity shows a result which was even greater than the dry LDPE T-Peel adhesive strength.

Thus, the range of adhesive strength retained by the gel-adhesive composite may exceed the adhesive strength of the adhesive alone and at the very least ranges from about 40% to about 500% of the adhesive strength of the adhesive alone.

A useful feature of the gel-adhesive composites of the present invention is the apparent near transparency of the composite, notwithstanding the two

phase nature of that composition. Because the gel and the pressure sensitive adhesive may be chosen from candidates having nearly identical indices of refraction, it is possible to achieve an at least nearly transparent composite. A nearly transparent composite enables the practitioner to use this coating as an adhesive for incise drapes or for other purposes which call for translucency approaching transparency. An incision area must be seen through the adhesive, and a composite of the present invention provides significantly improved utility over other adhesives.

While not being bound to any particular theory, it is believed that the near transparency of the composites of the present invention is directly related to the scattering of light caused by the dispersed gel particles 30 in the continuous adhesive 20. The amount or degree of scattering is related to four physical properties: differences in indices of refraction of the various components in the composite, particle size of the gel particles, the weight fraction of the gel particles in the continuous adhesive, and the thickness of the composite.

The difference in the indices of refraction between the pressure sensitive adhesives and the gels of the composite may be as small as 10 percent. In the case of acrylate adhesives and gels of poly (N-vinyl lactams) swollen with glycerol the difference in indices of refraction may be as small as 5 percent, desirably as small as 2 percent and preferably as small as 1 percent to provide a nearly transparent composite.

Further, if the gel particles 30 are larger than the wavelengths of visible light, i.e., greater than 1 micron, then Rayleigh scattering can also be minimized.

Light scattering is also reduced by smaller weight fractions of the gel particles 30 in the adhesive 20, e.g., 30 percent versus 50 percent and the thinner coatings of layer 10 applied to the skin, e.g. 50 microns

versus 100 microns. But these factors must be balanced against the need for strong adhesion and high moisture vapor transmission rate. Nonetheless, even with a weight fraction of gel particles 30 of as much as 95 weight percent dispersed in the adhesive 20 and coatings of the layer 10 of 100 microns thickness applied to the skin, the composites of the present invention can be nearly transparent.

While not intending to be an exhaustive treatment of the embodiments of the present invention, the following examples are illustrative of the scope of the invention which should not be limited thereto or thereby.

15

Example 1

Crosslinked Poly (N-vinylpyrrolidone) Hydrocolloid
Bulk Polymerization Using Photochemical Initiation

A solution composed of 0.32 parts
3,3'-ethylidene bis (N-vinyl-2-pyrrolidone), 1.0 parts
2-hydroxy-2-methyl-1-phenyl-1-propanone (serving as the photoinitiator) and 100 parts N-vinyl-2-pyrrolidone were placed in a flat dish at a thickness of 1.3 centimeters and was irradiated through a 0.5 centimeter thick quartz plate with a "Sylvania^R Sunlamp #052", from GTE Sylvania, Inc., Manchester, N.H., placed at a distance of 40 centimeters for about 20 minutes. The resultant crosslinked poly (N-vinylpyrrolidone) product was ground into a powder of particle size less than 0.25 centimeters using a blender and then thrice both emulsified in water and reprecipitated in acetone to remove residual monomers. The polymer was dried in a vacuum oven at 65°C. The polymer was then again ground into a fine powder using a commercially available grinder, a
"Brinkmann Retsch Grinder" from Brinkmann Instruments Company, Westbury, New York. The grinder was used at 20,000 rpm outfitted with a 750 micron grate to provide a

particle size distribution of 750 microns and smaller, with the majority (by weight percent) of particles between 25 and 200 microns in size. The hard hydrocolloid particles produced are available for swelling into the gel particles.

Example 2

Pressure Sensitive Adhesive Solution Polymerization

10

This was the pressure sensitive adhesive (PSA) used as the continuous matrix. It did not contain any gel. For this example, it was an isooctyl acrylate/N-vinyl pyrrolidone copolymer (91/9% weight) dissolved at 25% weight solids in a solvent blend of 50/50 heptane/ethyl acetate.

15

100.1 grams of isooctyl acrylate, 0.88 grams of ethanol, 164.6 grams of heptane, 164.6 grams of ethyl acetate, 9.9 grams of N-vinyl-2-pyrrolidone, and 0.294 grams of azobisisobutyronitrile were charged to a one pint bottle. The bottle was flushed with a stream of nitrogen for 3-4 minutes, sealed, and tumbled in a water bath at 55°C for 20 hours. The copolymer was formed and comprised 25% of the solution.

20

25

Example 3

Gel of Swollen Hydrocolloid-Percent Weight Ratio of Hydrocolloid to Swelling Agent of 1:19

30

Ten parts of the hydrocolloid polymer described in Example 1 were mixed with 190 parts of glycerol. This mixture was placed in a blender and sheared to maintain the small particle size of the gels, around 25 to 200 microns, by reducing agglomeration of the gel particles. The gel particles were prepared for dispersing into the pressure sensitive adhesive.

35

Example 4

Gel-Adhesive Composite with 10% Gel

5 To 50 parts of the pressure sensitive adhesive
solution described in Example 2 was added 1.39 parts of
gel of Example 3 and 2.09 parts of n-heptane and 2.09
parts of ethyl acetate. The mixture was mixed vigorously
with a Laboratory Dispersator, Series 2000 model 84,
commercially available from Premier Mill Corporation,
10 Reading, Pennsylvania, for several minutes until the gel
appeared evenly dispersed. The mixture was allowed to
set one minute to allow bubbles to eliminate from the
solution and the liquid was coated on a "Poly Slik
S-8003" silicone release liner available from H.P. Smith
15 at a thickness of 330 microns (13 mils). The coating was
dried 15 minutes at room temperature conditions and then
15 minutes at 79°C. The dried adhesive was then
laminated at a pressure of about 3.5 Kg/cm² to a
segmented block polyester film, prepared from "Hytrel"
20 4056" polyester elastomer available commercially from
DuPont de Nemours Company, Wilmington, Delaware. The
film thickness was 28 microns.

Example 5

25 Another Composite-25% Gel

To 50 parts of the adhesive solution described
in Example 2 was added 4.17 parts of the gel particles of
Example 3, 6.26 parts of n-heptane and 6.26 parts of
30 ethyl acetate. The mixture was prepared, coated and
laminated in accordance with Example 4.

35

Example 6

Another Composite-50% Gel

5 To 50 parts of the adhesive solution described in Example 2 was added 12.50 parts of the gel particles of Example 3, 18.75 parts of n-heptane and 18.75 parts of ethyl acetate. The mixture was prepared, coated and laminated in accordance with Example 4.

Example 7

Another Composite-75% Gel

10 To 30 parts of the adhesive solution described in Example 2 was added 22.50 parts of the gel particles of Example 3, 3.75 parts of n-heptane and 3.75 parts of ethyl acetate. The mixture was prepared, coated and laminated in accordance with Example 4.

20 The foregoing examples 4-7 illustrate the effect that the weight percent of gel, dispersed in an acrylic pressure sensitive adhesive, had on moisture vapor transmission rates (MVTR) of the composite. The results are shown in Table 1. The MVTR for each sample of the composite was determined using a variation of a
25 ASTM method E96-80. The film was placed adhesive side down over the opening of a standard glass vessel half filled with deionized water. The MVTR was determined by first allowing the sample 24 hours to equilibrate to the test conditions of 39°C and 20% ambient relative humidity
30 and then measuring the weight loss in the following 24 hours. The results described in Table 1 demonstrate a dramatic increase in the MVTR of the laminate.

35 To more fully understand the actual improvement made to the composite over the use of adhesive alone, the MVTR for the composite was mathematically segregated.

The following expression was used for calculating the MVTR of a two layer laminate of polymeric film and the composite.

5
$$1/\text{MVTR (film)} + 1/\text{MVTR (composite)} = 1/\text{MVTR (laminate)}$$

 The MVTR of the film alone was also determined in order to solve the equation. Since the effect of higher coating weights will reduce the MVTR, the results have been normalized to the same coating weight in order for more meaningful comparisons to be made. These results demonstrate a very dramatic rise in MVTR by the various composites over the MVTR shown for the pressure sensitive adhesive alone.

15

20

25

30

35

TABLE I

Example	Weight Fraction Ratio of PSA: Hydrocolloid: Swelling Agent	Coating Weight mg/cm ²	Water Loss in 24.5 hr (g)	Laminate MVTR g/m ² /24 hr	Composite MVTR g/m ² /24 hr	Normalized Composite MVTR	% Increase in MVTR
2	100 : 0 : 0	11.1	0.190	367	489	489	—
4	90 : 0.50 : 9.5	9.7	0.240	464	677	586	20
5	75 : 1.25 : 23.75	10.2	0.293	566	918	896	83
6	50 : 2.50 : 47.5	6.7	0.467	903	2329	1412	189
7	25 : 3.75 : 71.25	24.0	0.423	818	1836	3961	710
Film of							
Hytrel ^R 4056	—	0	0.763	1475	—	—	—

The results shown in Table I demonstrate a dramatic improvement in the normalized MVTR of the composites of Examples 4-7 over the MVTR of the pressure sensitive adhesive alone. As the last column demonstrates, in the composite where the pressure sensitive adhesive is an acrylate/N-vinyl-2-pyrrolidone copolymer (IOA/NVP) and the hydrocolloid is poly N-vinyl-2-pyrrolidone (PNVP), the MVTR increased rapidly with increased percentage by weight of the PNVP swollen with glycerol into a gel. Between almost 200 and 700 percent improvement was achieved by incorporating between 50 and 75 weight percent of gel in the composite. Less than 6% of the gel was hydrocolloid, demonstrating significant MVTR with a high loading of swelling agent in the gel: a ratio of hydrocolloid to swelling agent of 1:19 (1.25:23.75).

Examples 8-17

Determination of Relative Skin Adhesion Using Another Composite Formulation

Consequential to the dramatic improvement in MVTR, it was important to know what change in skin adhesion had occurred at these high gel loadings in the composite and the high weight percent ratio of swelling agent to hydrocolloid in the gel. A central composite design was utilized to assess the influence on skin adhesion of the gel weight fraction in the composite over the range of 0-50% and percent hydrocolloid in the gel over the ratios of 1:20 to 1:1. The hydrocolloid of Example 8 was used in the following formulations, examples 9-17.

-46-

Example 8

Crosslinked PNVP Hydrocolloid

5 A solution consisting of 0.16 parts of 3,3'-
ethylidene bis (N-vinyl-2-pyrrolidone), 1.0 parts
2-hydroxy-2-methyl-1-phenyl-1-propanone, (serving as the
photoinitiator) and 100 parts of N-vinyl-2-pyrrolidone
was polymerized and processed in the manner described in
Example 1.

10

Example 9-17

Example formulations 9-17 were prepared by the
following procedure. The cross-linked poly (N-vinyl
15 pyrrolidone) samples of Example 8 in the various weights
shown in Table II were first swollen in a solution of
glycerol and water in the parts by weight shown in Table
II to achieve approximately 5% PNVP polymer solids,
providing a weight ratio of 1:20. This produced a thick
20 gel paste which was easily dispersible.

The various gel particles of Examples 9-17 were
sheared with a "Laboratory Dispersator" mixer into a
mixture of the pressure sensitive adhesive prepared
according to Example 2.

25 An additional 20 parts by weight of n-heptane
was then added as the mixture was sheared vigorously for
between 5 and 10 minutes using a "Laboratory Dispersator"
mixer. Following shearing, the mixture was allowed to
stand one minute to eliminate bubbles from the solution
and was coated on the H.P. Smith "Poly Slik S-8003" brand
30 release liner. The composite was dried 10 minutes at
room temperature and oven dried at 93° C for one hour to
remove the volatile n-heptane and ethyl acetate and the
water from the gel and adhesive in the composite.

35

TABLE II

Gel and Composite Formulation (Parts by Weight)

	Example	Glycerol	Deionized		PNVP of PSA of		Composite
			Water		Ex. 8	Ex. 2*	Coating mg/cm ₂
5	2	0	0		0	100.0	5.2
	9	1.08	15.32		0.82	98.1	4.1
	10	1.68	2.72		0.22	98.1	3.4
	11	3.85	73.15		3.85	92.3	2.5
10	12	5.58	36.82		2.12	92.3	3.4
	13	5.58	36.82		2.12	92.3	3.6
	14	7.31	0.49		0.39	92.3	4.6
	15	8.89	127.31		6.81	84.3	4.3
	16	13.88	22.52		1.82	84.3	6.6
15	17	14.50	95.50		5.50	80.0	4.0

* The PSA weight is one quarter of the amount in this column because it is a 25% solution of PSA solids.

20 Two coated adhesive samples of each of the above examples were removed from the release liner and were hot laminated at 93°C and 3.5 Kg/cm² pressure to two different films, 28 microns thick, prepared from "Hytrel 4056" and "Hytrel 3548" brand polyester elastomers

25 commercially available from DuPont.

Skin adhesion of the samples laminated with film prepared from "Hytrel 4056" polyester elastomer was measured initially, after four hours and after 24 hours.

30 The following protocol was used. The backs of six subjects were first wiped clean with a 70:30 solution of isopropanol:water. Once the alcohol had dried, six samples, per formulation, 1.3 centimeters by 10 centimeters, were applied to each subject's back.

35 Two tapes of each formulation were removed per removal time using a 180 degree peel at 30.5 centimeters per minute at T₀ (within ten minutes of application), T₄

-48-

(after four hours), and T_{24} (after 24 hours). Then results of both samples for each time interval were averaged and reported as grams per centimeters in Table III.

5 The second skin panel test evaluated skin adhesion to sweaty skin using samples of Examples 2, 9-17 laminated to "Hytrel 3548" film prepared from polyester elastomer. The skin was not prepped with alcohol.

10 Two samples, per formulation, 1.3 centimeters by 10 centimeters were applied, to each of six subjects having dry skin. The subjects road a stationary bicycle for ten minutes in order to begin sweating. Two more samples were applied to the subjects' now wet back. The subjects then road the bike for 20 additional minutes, to
15 continue sweating. Following this time, all of the samples were removed in the same manner at 180 degree peel at 30.5 centimeters per minute. The 180° peel force results were averaged and reported in Table III as applied to dry skin and applied to wet skin. An
20 additional and noteworthy observation was that in none of the samples was there edge lift or, with one exception, any residue left on skin.

25

30

35

TABLE III
SKIN ADHESION

Example	Weight Fraction Ratio PSA:Hydrocolloid:Swelling Agent	180° Peel Strength			180° Peel Strength		
		T ₀ g/cm	T ₄ Hours		T ₂₄ Hours	Applied	
			g/cm	g/cm		Dry	Wet
2	100 : 0 : 0	62	103	114		53	45
9	92.8 : 3.1 : 4.1	52	87	102		54	43
10	92.8 : 0.8 : 6.4	52	87	99		46	40
11	75 : 12.5 : 12.5	49	83	109		47	42
12	75 : 6.9 : 18.1	47	88	98		45	34
13	75 : 6.9 : 18.1	50	85	100		43	35
14	75 : 1.25 : 23.75	51	91	94		47	37
15	57.3 : 18.5 : 24.2	42	82	80		40	34
16	57.3 : 5 : 37.7	63	96	52*		56	41
17	50 : 13.75 : 35.25	49	89	84		49	41

* Trace of glycerol residue

-50-

It is apparent that the incorporation of 25% weight fraction of gel to the composite (Examples 11-14) had only a slight impact on skin adhesion of the composite. Even levels of 50% weight fraction of gel (Example 17) resulted in little change to the skin adhesiveness of the composite of various weight fractions. Skin adhesiveness did not vary considerably whether applied dry, applied wet, or maintained on the skin for a few minutes, four hours, or one day.

Equally surprising was that residuing and lifting was not a problem, except for Example 16 which left a trace of glycerol residue, and even then only after 24 hours of continuous use.

These results confirmed that this composite truly incorporated the MVTR benefits of gel polymers with almost no degradation in adhesive performance of acrylate adhesives.

Examples 18-21

Incorporation Of Antimicrobial Agents Into The Composites

The purpose of the following examples 18-21, was to demonstrate the dramatic increase in antimicrobial activity even at relatively low loadings of gel, 25% by weight fraction of gel in the gel-adhesive composite, (i.e., excluding the weight of the antimicrobial agent until the weight fractions of gel-adhesive composite were determined.)

Controls were used for comparing the performance of the antimicrobial containing composite. These controls included "IobanTM 2" brand antimicrobial film, the adhesive thereof containing 2% iodine; "Opsite CHTM" brand incise drape, the adhesive thereof containing 5% chlorhexidine acetate; and "Steri-DrapeTM 2" incise drape, the adhesive thereof not containing an antimicrobial agent. "Ioban 2TM" and "Steri-DrapeTM 2"

-51-

brand incise drape are both commercially available from 3M Company, St. Paul, Minnesota. "Opsite CHTM" brand incise drape is commercially available from Smith and Nephew Medical Limited, Hull, HU32BN England.

5

Examples 18-21

10 These examples utilized the cross-linked poly (N-vinyl pyrrolidone) of Example 8 which was first swollen by a solution containing water, glycerol and antimicrobial (e.g. iodine and sodium iodide or chlorhexidine gluconate solution) in the parts by weight shown in Table IV.

15 The swollen gel paste was then dispersed into the acrylic adhesive solution of Example 2 with a "Laboratory Dispersator" mixer, vigorously for between 5 and 10 minutes until the gel was fully mixed. An additional 20 parts (wt.) of n-heptane is added to assist in the dispersion process. The solution was sheared for several minutes or until uniform and free of
20 agglomerates. The mixture was allowed to stand for one minute, to eliminate bubbles prior to coating on a H.P. Smith "Poly Slik S-8003" brand release liner. The composite was dried 10 minutes at room temperature and
25 then oven dried at 80°C for one hour. The coated adhesive samples were removed from the release liner and hot laminated at 93°C at 3.5 Kg/cm² pressure to 28 microns (1.1 mil) thick film prepared from "Hytrel^R 3548" brand elastomer.

30

35

-52-

TABLE IV
Gel and Composite Formulation (Parts by Weight)

Example	Glycerol	Distilled of Water	PNVP		NaI	20% CHg* PSA	
			Ex.8	Iodine		in Water	of Ex.2**
18	5.58	36.82	2.12	0.61	0.77	---	92.30
19	13.88	22.52	1.82	0.78	0.93	---	84.30
20	5.58	30.67	2.12	---	---	7.65	84.90
21	13.88	15.07	1.82	---	---	9.25	77.56

* 20% chlorhexidine gluconate in water.

** 25% weight percent of PSA solids in grams of PSA solution

Antimicrobial activity In Vitro testing results for the controls and the laminated composites of Examples 18-21 are presented in Table V below. The Ulrich procedure was used for the test, according to the procedure identified in Infection in Surgery, August 1984, 569-574, as modified below.

Ulrich Procedure For Determining Antibacterial Activity Of Transparent Dressings

Specimens were handled aseptically on a laminar flow clean bench which was disinfected with isopropanol prior to use. The laminated composites were each cut into one inch squares. Liner was removed with the aid of sterile forceps and the film backing placed coating-up on a raised surface in the bottom of a moist chamber.

Just prior to application, *Streptococcus faecalis* was grown on m-enterococcus agar. The suspension was adjusted turbidimetrically to contain at least 10^8 bacteria/ml and a viable count was made by the

-53-

pour-plate method. A micropipette was employed to deposit and distribute 0.05 ml of this suspension on the adhesive surface; the contents were first spotted over the entire surface and then spread evenly with the pipette tip.

At time intervals of 10, 30, 60, and 90 minutes the seeded squares were removed and separately placed in blenders containing 100 ml of 6.25 fold strength "Difco" brand neutralizing buffer commercially available from Baxter Health Care Corp. This concentration is not inhibitory for most bacteria and negates transfer of both antimicrobials to the rinsing fluid. The samples were essentially macerated by five minutes agitation at full speed. An aliquot of rinsing fluid was decanted from the blender cup and exponentially diluted in sterile physiological saline. The following dilutions were plated in m-enterococcus agar to provide viable counts: undiluted, 10^{-1} , 10^{-2} , 10^{-3} , 10^{-4} , 10^{-5} ; an initial dilution of 10^{-2} was imposed on these counts by the rinsing fluid. Plates were incubated overnight at 35°C and enumerated with the Biotran II automatic colony counter.

The \log_{10} reduction in bacterial numbers was determined by the numerical difference between the inoculum and recovery values. Duplicate platings on duplicate specimens were averaged to obtain final numbers.

-54-

TABLE V
IN VITRO ANTIMICROBIAL EFFICACY
Log Reduction (*S. faecalis*)

Example	Weight Fraction Ratio PSA:Hydrocolloid:Swelling Agent	Antimicrobial	Ulrich Procedure			
			Antimicrobial Activity			
			10 min	30 min	60 min	90 min
18	75 : 6.88 : 18.12	2% Iodine	1	5	—*	4
19	57.3 : 5 : 37.7	2% Iodine	Nil	3	—*	6
20	73.4 : 7.3 : 19.3	5% Chlorhexidine	3	5	—*	5
21	55.25 : 5.2 : 39.55	5% Chlorhexidine	2	2	—*	6
"Ioban™ 2" Anti- microbial Film	—	2% Iodine	Nil	3	5	5
"OPSITE™ CH" Drape	—	5% Chlorhexidine	0	—*	0	—*
"STERI-DRAPE™ 2" Drape	—	(NO ANTIMICROBIAL)	0	0	—*	0

*Not measured

-55-

The results indicate that chlorhexidine did not appear to be active in the "OpsiteTM CH" incise drape control but was very active in the composite of Example 20 and 21. Iodine was very active from the "IobanTM 2" antimicrobial film control, but the composite of Examples 18 and 19 showed comparable iodine activity.

Examples 22-33

The next Examples 22-33 demonstrated the broad flexibility in formulating these gel-adhesive composites. Table VI shows the formulations of the composites in parts by weight having the antimicrobial agent therein.

The procedure for preparing these examples was the same as that outlined in Examples 18-21, except that the percent of PSA solids was slightly higher resulting in recalculation of the weight fraction of the PSA in the final composite.

TABLE VI
Gel and Composite Formulations (Parts by Weight)

	Example	Glycerol	Distilled Water	PNVP of Ex. 8	20% CHg* in water	PSA (27.6% solids) of Example 2
25	22	0.85	14.55	0.77	3.7	58.38
	23	2.15	14.65	0.84	3.9	57.02
	24	1.41	29.99	1.57	3.9	66.95
	25	5.69	22.71	1.42	4.6	52.88
30	26	3.74	63.89	3.38	4.6	52.88
	27	3.74	63.89	3.38	4.6	52.88
	28	3.74	63.86	3.38	4.6	52.88
	29	3.74	63.86	3.38	4.6	52.88
	30	1.78	105.02	5.34	4.6	52.88
35	31	9.40	63.93	3.67	5.6	46.93
	32	4.32	170.71	8.75	5.6	46.93
	33	8.59	146.81	7.77	6.1	43.64

* 20% chlorhexidine gluconate in water.

Table VII demonstrated that even as the weight fraction of the gel was varied from 10-60%, acceptable adhesion and in most cases superior antimicrobial gel-adhesive composites were possible.

5

10

15

20

25

30

35

TABLE VII
In Vitro Test vs. strep. faecalis (ATCC 10741)
And Skin Adhesion

Example	Weight Fraction Ratio PSA:Hydrocolloid:Swelling Agent	180° Peel Strength			Ulrich Procedure	
		T ₀ Hour g/cm	T ₁ Hour g/cm	T ₆ Hour g/cm	Antimicrobial Activity 6 min	Antimicrobial Activity 10 min
22	90.9 : 4.3 : 4.8	45.9	81.1	97.1	1.0	5.0
23	84 : 4.5 : 11.5	46.1	78.3	82.5	2.0	5.0
24	86.1 : 7.3 : 9.0	43.9	74.9	82.8	2.0	5.0
25	67.3 : 6.5 : 26.2	51.6	84.9	101.0	2.0	4.0
26	67.2 : 15.6 : 17.2	45.6	66.1	79.1	2.0	5.0
27	67.2 : 15.6 : 17.2	45.4	66.2	79.2	2.0	5.0
28	67.2 : 15.6 : 17.2	45.4	66.8	79.8	2.0	5.0
29	67.2 : 15.6 : 17.2	45.4	66.1	78.7	2.0	5.0
30	67.2 : 24.6 : 8.2	20.8	36.1	61.8	2.0	5.0
31	49.8 : 14.1 : 36.1	42.8	78.0	86.6	3.0	5.0
32	49.8 : 33.6 : 16.6	14.6	25.8	43.9	1.0	5.0
33	42.4 : 27.4 : 30.2	31.9	56.9	73.2	2.0	3.0
"Ioban™ 2"	100 : 0 : 0	54.8	71.1	88.6	Nil	<1.0

Antimicrobial Film

As can be seen by referring to Table VII, there was no significant variance among the various gel-adhesive composites as to the antimicrobial activity. Indeed throughout a broad range of weight fractions of the gel, the antimicrobial activity was consistently excellent and compares favorably with "IobanTM 2" brand antimicrobial film, which is an iodine antimicrobial incise drape without gel therein.

Examples 34-44

Necessity Of Hydrocolloid And Non-Volatile Swelling Agent

The following examples illustrate the importance of swelling the hydrocolloid with a non-volatile swelling agent. Example formulations 35, 36, 39, and 40 were prepared by the same procedure as outlined for Examples 9-17, according to the formulations identified in Table VIII, with the exception that the coatings were dried 30 min. at 22°C followed by oven drying for 20 min. at 80°C. Example formulations 37, 38, 41, and 42 were prepared according to the same procedure as Examples 35, 36, 39, and 40, except that in the formulation of the hydrocolloid, no crosslinking agent was used. Example 34 was a repeat example of pressure sensitive adhesive, and Example 44 was a comparison example mixing the swelling agent without hydrocolloid into the adhesive.

TABLE VIII
Gel and Composite Formulations (Parts by Weight)

Example	Glycerol	Deionized Water	Crosslinked Hydrocolloid of Example 8	Linear PNVP (360,000 M.W.)	PSA (28% Solids) of Example 2	Heptane
34	0	0	0	0	50.0	0
35	7.0	30.5	3.0	0	107.1	20.3
36	14.0	61.0	6.0	0	71.4	21.4
37	7.0	5.0	0	3.0	107.1	29.5
38	14.0	10.0	0	6.0	71.4	35.5
39	0	0	5.0	0	53.6	21.1
40	0	0	5.0	0	35.7	19.3
41	0	0	0	5.0	53.6	10.8
42	0	0	0	5.0	35.7	19.3
43	10.0	0	0	0	107.1	22.2
44	20.0	0	0	0	71.4	19.7

The dried adhesives were hot laminated at 93°C to 28 micron (1.1 mil) thick film prepared from "Hytrel^R 4056" brand elastomer film. These samples were evaluated for T-Peel adhesion to 20 micron thick low density polyethylene film. Moisture vapor transmission rates were also determined in the same manner as described in Examples 4-7. The results are reported in Table IX below.

T-peel tests were performed on each sample by using a variation of ASTM D 1876 on an Instron Model 1122 stress analyzer. The samples were cut to 2.54 cm by 10.2 cm, removed from the release liner, and laminated with a 2.25 Kg roller onto 20 micron thick low density polyethylene (LDPE) film. Six samples for each test were made and tested, the averaged values were reported. The samples were tested under two sets of conditions. The first set of conditions was to age the samples 10 days at room temperature (22°C) prior to testing. The second set of conditions was to age the samples at 50% relative humidity and 21°C for 6 days. The jaw separation speed on the Instron Model 1122 stress analyzer was 25.4 cm/min.

5	10	15	20	25	30	35
TABLE IX						
Weight Fraction Ratio						
PSA:Hydrocolloid:Swelling Agent						
Example	T-Peel Adhesion (g/cm)		Laminate MVTR			
	LDPE	LDPE	g/m ² /24 hours			
	22°C	21°C/50R.H.				
34	68	59	408			
35	68	63	619			
36	80	114	797			
37	54	52	856			
38	68	79	1066			
39	66	61	800			
40	23	20	N/A*			
41	45	38	988			
42	11	25	N/A*			
43	61**	59**	533			
44	66**	70**	1001			
Film of "Hytrel" ^R						
4056" brand						
polyester elastomer —						
						1376

* Samples without defects to the adhesive could not be made.

** Surface of sample showed glycerol residual which bloomed to the surface.

Examples 35 and 36 utilized crosslinked PNVP hydrocolloid while Examples 37 and 38 utilized uncrosslinked PNVP hydrocolloid. By comparison, Examples 35 and 38 utilized non-volatile glycerol while Examples 39-42 utilized no swelling agent, with a further comparison of crosslinked hydrocolloids in Examples 39 and 40 and uncrosslinked hydrocolloids in Examples 41 and 42. Finally, Examples 43 and 44 used no hydrocolloid with unacceptable results footnoted.

The use of a swelling agent in the gel (Examples 35-38) allowed the composite to substantially retain or even increase the adhesiveness of the pressure sensitive adhesive. For example, the T-Peel adhesive strength on LDPE at 22°C of Example 36 is greater than the IOA/NVP PSA of Example 34, the unswollen stoma-type adhesives of Example 39 and 40 using crosslinked PNVP hydrocolloid, and the unswollen stoma-type adhesives of Examples 41 and 42 using uncrosslinked PNVP hydrocolloid. A comparable favorable result was obtained after aging in humid conditions. And MVTR was nearly twice the amount as that of the PSA alone of Example 34. The comparative results for Examples 35, 37 and 38 were not as dramatic. But generally the adhesive strength of these Examples were comparable to the pressure sensitive adhesive of Example 34 and the MVTR is 150-175% percent greater.

Table IX also shows the comparison of crosslinked PNVP vs. uncrosslinked PNVP both swollen into a gel and unswollen as a hydrocolloidal material in a stoma-type adhesive. The T-Peel strength on LDPE results were greater for crosslinked PNVP than the uncrosslinked PNVP, both in dry and for humid conditions. Thus, crosslinked PNVP is preferred to uncrosslinked PNVP. Examination of the MVTR results of crosslinked and uncrosslinked PNVP showed that uncrosslinked PNVP and crosslinked PNVP are acceptable and superior to the adhesive of Example 34.

-63-

Table IX also shows the unacceptable results of the attempt to formulate a composite without the presence of hydrocolloid. Examples 43-44 showed the effects of incompatible blooming of the glycerol to the surface of the composition, an unacceptable condition. Further, these adhesion values shown for Examples 43-44 will fall dramatically as the composite ages and more glycerol blooms to the surface.

Examples 45-53

10

Composites Prepared From A Latex Of Hydrophobic PSA In An Aqueous Solution

These examples utilized a latex base PSA, such that the hydrocolloid was placed in the continuous water phase. The examples demonstrated the superior MVTR performance of composite prepared by this technique and the importance of the swelling agent to the composite.

The formulations were prepared by first swelling the PNVP in the glycerol and water. The swollen gel was then blended into a PSA latex ("Rhoplex^R E-1960D 53.0% N.V.", available from Rohm & Haas Co. Philadelphia, PA) by a "Laboratory Dispersator" mixer from Premier Mill Corporation. The final non-volatiles were calculated and a coating thickness was estimated to produce 80 microns of dried composite. The samples were coated on release liner and dried at 22°C for 30 min followed by 20 min. at 80°C. The dried composite was hot laminated at 93°C to 28 micron thick film prepared from "Hytrel^R 4056" brand polyester elastomer. Specific formulations in the latex are identified in Table X, and T-Peel strength and MVTR results, measured in the same manner as for Examples 34-44 are reported in Table XI.

35

TABLE X
Gel and Composite Formulations (Parts By Weight)

Example	Deionized		PNVP of Example 8	PNVP (360,000 M.W.)	53% Solids	
	Glycerol	Water			"Rhoplex" ^R	E-1960D [®] Latex
45	0	0	0	0	50.0	
46	7.0	45.1	3.0	0	56.6	
47	14.0	58.3	6.0	0	37.7	
48	7.0	33.4	0	3.0	56.6	
49	14.0	42.3	0	6.0	37.7	
50	0	35.1	2.5	0	14.2	
51	0	48.4	5.0	0	9.4	
52	0	12.0	0	5.0	28.3	
53	0	18.0	0	5.0	9.4	

Film of "Hytrel[®] 4056"
brand polyester elastomer

35
30
25
20
15
10
5

TABLE XI

Example	Weight Fraction Ratio PSA:Hydrocolloid:Swelling Agent	T-Peel Adhesion (g/cm)			Laminate MVTR g/m ² /24 hours
		LDPE	LDPE	21°C/50R.H.	
		22°C			
45	100 : 0 : 0	66	95	619	
46	75 : 7.5 : 17.5	75	98	948	
47	50 : 15 : 35	127	198	1442	
48	75 : 7.5 : 17.5	39	139	928	
49	50 : 15 : 35	80	93	1350	
50	75 : 25 : 0	13	4	1178	
51	50 : 50 : 0	0	0	1211	
52	75 : 25 : 0	0	0	1205	
53	50 : 50 : 0	0	0	1198	
Film of "Hytrel" ^R					
4056" brand					
polyester Elastomer					
		---	---	1376	

Examples 46 and 47 demonstrated the use of swollen gel of crosslinked PNVP. Examples 48 and 49 demonstrated the use of swollen gel of uncrosslinked PNVP. Examples 50 and 51 demonstrated the use of gel of crosslinked PNVP temporarily swollen by water. Examples 52 and 53 demonstrated the use of gel of uncrosslinked PNVP temporarily swollen by water.

Again, a comparison of the T-Peel strength on LDPE of the various examples with LDPE aged in dry and wet conditions demonstrated the superior performance of the composites prepared using a non-volatile swelling agent and a crosslinked PNVP hydrocolloid, i.e., Examples 46 and 47. Of the compositions of Examples 50-53 without the non-volatile swelling agent, only the composition of Example 50 has any T-Peel adhesion at all, which amount was vastly inferior to the results for any of the compositions of Examples 46-49.

As shown in Table XI, excellent MVTR was provided by the compositions of Examples 46-49, between 1.5 and 2.0 times the MVTR provided by latex-produced PSA of Example 45. While other Examples also had a high MVTR compared with the latex-produced PSA of Example 45, none of them also provided higher T-Peel adhesive strengths than the composite of Example 47.

Data in Table XI also demonstrated by comparison to the data of Table IX that the T-Peel strength of the preferred composites were not adversely affected by the method of preparation of the composite. Whether dispersed into a continuous hydrophobic phase, the results of which are reported in Table IX, or mixed into a hydrophilic latex, the results of which are reported in Table XI, the composites of the present invention provided excellent adhesive strength and high moisture vapor transmission rates.

Examples 54-59

Gel Particle Size Variations On The Composites

5 The influence of particle size on adhesion and
MVTR was studied. The PNVP particles were prepared by
grinding the hydrocolloid polymer of Example 8 through a
"Retsch Brinkman" grinder at 20,000 rpm and with a 3/4 mm
grate. The particles were then sized through several
10 wire meshes to provide 3 samples ranging from 25-106
microns, 106-212 microns and 300-600 microns. Due to the
very fragile nature of the swollen gels during
processing, great care was taken to use minimal shear in
blending them into the adhesive latex. With this
exception, the Examples of 54-59 were prepared in the
15 same manner as for Examples 45-53. Table XII reports the
formulations and Table XIII reports the T-Peel adhesive
strength and MVTR of each composite of the Examples, as
measured in the same manner as that for Examples 35-44.

20

25

30

35

TABLE XII
Formulations of Gel and Composite (Parts by Weight)

Example	Particle Size Range of PNVP of Ex. 8	Deionized		PNVP of Ex. 8 (sized)	53% Solids "Rhoplex" E-1960D" Latex
		Glycerol	Water		
54	300-600 microns	7.0	53.0	3.0	56.6
55	300-600 microns	14.0	76.0	6.0	37.7
56	106-212 microns	7.0	43.0	3.0	56.6
57	106-212 microns	14.0	76.0	6.0	37.7
58	25-106 microns	7.0	43.0	3.0	56.6
59	25-106 microns	7.0	38.0	3.0	18.9

Example	Dried Hydrocolloid Particle Size	Weight Fraction Ratio of PSA:Hydrocolloid:Swelling Agent	T-Peel (g/cm)		Laminate MVR g/m ² /24 hour
			LDPE	LDPE	
			22°C	21°C/50R.H.	
54	300-600 microns	75 : 7.5 : 17.5	148	152	889
55	300-600 microns	50 : 15 : 35	125	130	1067
56	106-212 microns	75 : 7.5 : 17.5	291	270	790
57	106-212 microns	50 : 15 : 35	168	148	1106
58	25-106 microns	75 : 7.5 : 17.5	248	273	856
59	25-106 microns	50 : 15 : 35	164	150	1310
45	No Hydrocolloid	100 : 0 : 0	66	95	619
Film of "Hytrel ^R /4056"					
brand polyester elastomer					
		0	—	—	1376

TABLE XIII

-70-

The results as reported in Table XIII did not demonstrate a definite particle size performance relationship to adhesion. At the 50:15:35 weight fraction ratio (Examples 55, 57, and 59) MVTR increased as the particle size decreased from 300-600 microns to 25-106 microns. However, for composites with less gel dispersed in the adhesive matrix (Examples 54, 56, and 58), even at the same ratio of hydrocolloid to swelling agent, there was no trend between particle size and MVTR.

Examples 60-64

Other Hydrocolloids In The Gel-Adhesive Composites

The previous examples have all focused on linear or crosslinked poly (N-vinyl pyrrolidone) hydrocolloids swollen with a non-volatile swelling agent. The following examples incorporate two variations in the scope of the invention, a change in the hydrocolloid and a change in the continuous pressure sensitive adhesive matrix.

Example 60

Pressure Sensitive Adhesive

This example described a pressure sensitive adhesive blend used as the continuous matrix. The adhesive was composed of 50.0 parts "Krayton^R 1111" brand styrene-isoprene block copolymer from Shell Chem. Co., Houston, Texas and 70.0 parts "Wingtac^R 95" brand polyterpene resin from Goodyear Tire and Rubber, Akron, Ohio dissolved in 360.0 parts of toluene. The hydrophobic adhesive blend was dissolved in a solvent which phase separated from water.

-71-

Example 61

Guar Gum Hydrocolloid

5 To 0.9 parts of guar gum ("Uniguar^R 150" brand
guar gum manufactured by Hi-Tek polymers, Clifton, NJ)
was added 2.1 parts glycerol. The guar gum solution was
heated for 2 hours at 65°C to enhance the absorbance of
glycerol. The swollen gel was mixed vigorously with a
"Laboratory Dispersator" mixer with 36.0 parts of Example
10 60, until the gel appeared evenly dispersed. The mixture
was allowed to stand for one minute for bubbles to
escape. The composite was coated on release liner at a
thickness of 0.38 mm. The composite was dried 30 min. at
22°C and 15 min. at 88°C.

15 The dried composite was then hot laminated at
93°C to 28 microns thick film prepared from "Hytrel^R
4056" brand elastomer.

Example 62

Xanthan Gum Hydrocolloid

20 To 0.9 parts of Xanthan Gum ("Keltrol^R" brand,
manufactured by Merck and Co., Inc. San Diego, CA) was
added 2.1 parts glycerol and the mixture heated for 2
hours at 65°C to allow the glycerol to swell the xanthan
25 gum. The swollen gel was mixed vigorously as in Example
61 with 36.0 parts of Example 60 until the gel appeared
evenly dispersed. The coating, drying and laminating
followed the steps of Example 61.

30

Example 63

Hydroxypropyl Methyl Cellulose

35 To 0.9 parts of Hydroxypropyl Methyl Cellulose
(HPMC) ("Methocel^R J75MS" brand HPMC, manufactured by Dow
Chemical, Midland, MI) was added 2.1 parts glycerol and
0.53 parts deionized water and the mixture was heated at

-72-

65°C for 2 hours to allow the glycerol to swell the HPMC. The mixture was mixed with 36.0 parts of the adhesive of Example 60 vigorously as in Example 61 until the gel appeared evenly dispersed. The coating, drying, and laminating followed the steps of Example 61.

Example 64

Alginate

To 2.0 parts sodium Alginate ("Kelgin^R MV" brand, alginate manufactured by Merck & Co, Inc., San Diego, CA) were added 2.5 parts CaSO_4 , 0.8 parts Na_3PO_4 , 20.0 parts glycerol and 60.0 parts deionized water. The sample was mixed and allowed to stand for several hours to form a firm gel. The gel was placed in a "Waring" 700 Model #31BL46 brand blender and ground at the uniform speed of the blender to produce small particle sized gels of less than about 200 microns. 67.3 parts of the gel particles were then mixed with 80.0 parts of the adhesive of Example 60 vigorously as in Example 61 until the gel appeared evenly dispersed. The coating, drying and laminating followed the steps of Example 61.

T-Peel and MVTR results for the composites of Examples 60-64 are reported in Table XIV.

-73-

Example	Hydrocolloid	Weight Fraction Ratio of PSA:Hydrocolloid:		T-Peel (g/cm)		Laminate MVTR g/cm ² /24 hr	Dried Coating wt. mg/cm ²	MVTR Normalized to 6.64 mg/cm ² Coating wt.
		Swelling Agent		LDPE				
		22°C	21°C/50R.H.	LDPE	LDPE			
60	None	100 : 0 : 0	200	232	158	3.33	84	
61	Guar Gum	75 : 7.5 : 17.5	284	307	336	5.79	328	
62	Xanthan Gum	75 : 7.5 : 17.5	166	105	356	7.64	393	
63	HPMC	75 : 7.5 : 17.5	182	245	138	7.76	159	
64	Alginate	53.5 : 4.3 : 42.2	218	279	375	9.87	492	

TABLE XIV

Table XIV demonstrated that the T-Peel adhesive strength of a variety of hydrocolloids was in the range of acceptable PSA T-Peel strengths in both dry and wet conditions. But the MVTR of the composites of Examples 61-64 were significantly greater than the PSA of Example 60. Thus, a variety of hydrocolloids were acceptable in the gel-adhesive composite of the present invention.

Examples 65-71

Other Gel-Adhesive Composites Having Large Weight Fractions Of Gel Therein

The following examples demonstrated the amount of swollen gel which can be dispersed into the pressure sensitive adhesive matrix before the adhesion of the resulting composite suffers. Example formulations 65-70 were prepared by the same procedures outlined in examples 34-44 with the exception that the composites were air dried 15 min at 22°C and oven dried at 100°C for 2 hours. Example 71 was mixed and pressed to a thickness of 0.22 mm and laminated to 28 micron thick film prepared from "Hytrel^R 4056" brand polyester elastomer. T-Peel Adhesion to LDPE was measured under the same conditions as that used for Examples 34-44, in dry humidity at 22°C. Table XV identifies the formulations and Table XVI reports the results.

Example	Gel and Composite Formulations (Parts by Weight)					Dried Coating at mg/cm ²
	Glycerol	Deionized Water	PNVP of Ex. 1	PSA (25.0% solids) of Ex. 2	n-Heptane	
65	0	0	0	100.00	0	5.68
66	.75	2.50	.25	76.00	10.0	5.17
67	9.00	30.00	3.00	32.00	20.0	5.55
68	10.50	35.00	3.50	24.00	20.0	5.43
69	11.25	37.50	3.75	20.00	20.0	4.71
70	12.00	40.00	4.00	16.00	20.0	5.30
71	9.00	0	3.0	0	0	25

TABLE XVI

5	<u>Example</u>	Weight Fraction Ratio of PSA:Hydrocolloid:	T-Peel Adhesion
		<u>Swelling Agent</u>	<u>(g/cm) on LDPE</u>
	65	100 : 0 : 00	66
	66	95 : 1.25 : 3.75	63
	67	40 : 15 : 45	107
10	68	30 : 17.5 : 52.5	76
	69	25 : 18.75 : 56.25	68
	70	20 : 20 : 60	49
	71	0 : 75 : 25	8.5

15 As the percentage of PSA decreased, the T-Peel adhesion of the composite against LDPE rose and fell. Except for Example 65 containing no gel, the hydrocolloid:swelling agent weight fraction ratio for the other Examples 66-71 was a constant weight fraction ratio of 1:3. When considering only the results of T-Peel adhesion, the variation of only the weight fractions of the gel to the PSA demonstrated that a possible range of gel weight fractions was from about just greater than 0, about 5, (Example 66) to about 75 percent (Example 69), i.e., the weight fraction sum of the hydrocolloid and the swelling agent. At ratios of PSA/gels ranging from about 40:60 to about 25:75, (Examples 67-69), where the ratio of the hydrocolloid was constant at 1:3, the T-Peel adhesive strength in the gel-adhesive composite even exceeded the T-Peel adhesive strength of the PSA alone.

Examples 72-78

Other Gel Weight Fraction Ratio Limits

35 Example 30 demonstrated a useful formulation containing PNVP hydrocolloid to glycerol swelling agent ratio of 3:1 (24.6:8.2). The skin adhesion results for

Example 30 showed less peel adhesion than other compositions such as Examples 25-29 having the same weight fraction of gel in the composite but having a greater weight fraction of swelling agent in the gel.

5 The following examples demonstrated the acceptable and preferred ranges of the weight fraction ratios of hydrocolloid to swelling agent. T-peel adhesion results measured in the same manner as for Examples 34-44 to low density polyethylene (LDPE) are reported in Table XVIII below.

10 LDPE is not a perfect skin substitute for adhesion testing but does represent the general trends in adhesion. At a very high hydrocolloid/swelling agent weight fraction ratio, such as 42.5:7.5 or 5.7:1 (Example 15 78), the adhesive strength was comparable to unswollen hydrocolloids, i.e., see Example 40. Example formulations 72-78 were prepared by the same procedure outlined in examples 65-70 and are identified in Table XVII. T-Peel adhesive strength was measured in the same 20 manner as for Examples 65-71.

TABLE XVII

Gel and Composite Formulations (Parts by Weight)

Example	Glycerol	Deion- ized Water	PNVP of Ex. 8	PSA (25.0% solids)		Heptane	Coating wt mg/cm ²
				Ex. 2			
25	72	7.13	3.80	.38	30.0	10.0	5.36
30	73	6.75	7.50	.75	30.0	10.0	4.65
	74	6.00	15.00	1.50	30.0	10.0	4.97
	75	4.50	30.00	3.00	30.0	10.0	5.55
	76	2.00	30.00	3.00	20.0	10.0	5.62
	77	1.25	37.50	3.75	20.0	10.0	6.07
35	78	0.75	42.50	4.25	20.0	10.0	6.26

TABLE XVIII

5	<u>Example</u>	Weight Fraction Ratio of PSA:Hydrocolloid: <u>Swelling Agent</u>	T-Peel Adhesion (g/cm) on LDPE
	70	100 : 0 : 0	66
	72	50 : 2.5 : 47.5	99
10	73	50 : 5 : 45	80
	74	50 : 10 : 40	108
	75	50 : 20 : 30	68
	76	50 : 30 : 20	28
	77	50: 37.5 : 12.5	29
15	78	50: 42.5 : 7.5	25
	40	66.7 : 33.3 : 0	23

As illustrated in Table XVIII, the T-Peel strength also rose and fell throughout increasing weight fraction ratios of hydrocolloids to swelling agents. Based on the variation of such weight fraction ratios and a constant weight fraction of the swollen gel in the composite, a desirable range extended from about 1.5:1 to about 1:19 (Examples 72-76) with a preferable range for the better balance of properties being from about 1:1.5 to about 1:19 (Examples 72-75).

Examples 79-86Determination Of Acceptable Shear Modulus Of The Gel

The following examples 79-86 quantified the shear modulus range for the gels in the gel-adhesive composites of the present invention. The samples were prepared by mixing powdered poly (N-vinyl pyrrolidone) of example 8 with varying amounts of glycerol. The samples were allowed 24 hours to completely absorb the glycerol, followed by hydraulically pressing the samples between

release liners to a thickness of 1 mm. The resultant gel films were cut to 50 mm diameter circles and tested between 50 mm diameter parallel plates at 22°C on a "Rheometrics Mechanical Spectrometer", Model 605 manufactured by Rheometrics Inc. 1 Possumtown Road, Piscataway, NJ. These details and ASTM D 4065-82 describe the technique used. The Shear Modulus for each samples is reported Table XIX below in dynes/cm² at 1 and 5.6 Rad/sec.

TABLE XIX

Gel and Composite Formulations (Parts by Weight)
and Shear Modulus Results

Example	Weight %		Shear Modulus (Dynes/cm ² *10 ⁻³)	
	PNVP	Glycerol	1 Rad/Sec.	5.6 Rad/Sec.
79	5	95	2.95	5.13
80	10	90	7.20	10.32
81	20	80	16.94	26.24
82	30	70	25.22	42.24
83	40	60	41.17	74.19
84	50	50	153.5	179.7
85	60	40	999.4	2,068
86	75	25	6,171	6,423

Examples 30 and 77 having PNVP as the hydrocolloid showed useful formulations containing PNVP hydrocolloid/swelling agent ratios up to 3:1. Since the shear modulus of the gel will vary with the type of hydrocolloid (e.g. PNVP, alginates, cellulosics) and the choice of non-volatile swelling agent, examples 79-86 were important in defining a desired upper modulus. An upper modulus is desired to assure that the gel particles are soft and pliable in the composites.

There does not appear to be a lower modulus limit; rather there must be at least a minimal amount of hydrocolloid present to prevent the swelling agent from migrating or blooming to the surface of the composite and thereby degrading the adhesive properties thereof. An example of this incompatible blooming was shown by examples 44-45 where no hydrocolloid was present.

The desired upper shear modulus limit for the swollen hydrocolloid was represented by example 86, at 6.2×10^6 dynes/cm². The preferred upper shear modulus limit was represented by example 84 at 1.5×10^5 and the most preferred upper shear modulus limit was represented by example 83 at 41.2×10^3 dynes/cm².

Examples 87 and 88 Other Swelling Agents

Examples 87 and 88 demonstrated the use of other non-volatile swelling agents in place of glycerol.

Example 87

To 3.0 parts of crosslinked poly (N-vinyl pyrrolidone) of example 8 was added 7.0 parts propylene glycol and 30.5 parts of distilled water. Once the solution was absorbed by the PNVP, the gel was mixed vigorously with 35.7 parts of the PSA of example 2 (28.0% solids) and 10.7 parts n-heptane until the hydrocolloid appeared evenly dispersed. The coating, drying and laminating follow the procedure for example 65. The resulting gel-adhesive composite was transparent, very adhesive and had a smooth texture. T-peel adhesion to LDPE was 65 gm/cm, which compares favorably with the use of glycerol, as seen in Examples 6-69 and 72-75.

-81-

Example 88

To 3.0 parts of crosslinked poly (N-vinyl pyrrolidone) of Example 8 was added 1.0 parts glycerol, 8.6 parts of a 70% sorbitol solution in water and 30.5 parts distilled water. Once the solution was absorbed by the PNVP the gel was mixed vigorously with 35.7 parts of the PSA of Example 2 (28.0% solids) and 10.7 parts n-heptane until the hydrocolloid appeared evenly dispersed. The coating, drying and laminating followed the steps of Example 65. The resulting gel-adhesive composite was transparent, very adhesive and had a smooth texture. T-peel adhesion to LDPE was 66 gm/cm, which compares favorably with the use of glycerol, as seen in Examples 66-69 and 72-75.

In accordance with the Patent Statutes, embodiments of the invention have been described. A series of examples have been provided to illustrate the variety of acceptable components according to the scope of the invention. The invention is not to be limited by the description of the embodiments or examples. There are many variations within the scope of the invention. Consequently, for an understanding of the scope of the invention, reference is made to the following claims.

-82-

WHAT IS CLAIMED IS:

1. A composite of a gel dispersed in a pressure sensitive adhesive matrix, comprising:

5 (a) from about 5 weight percent to about 99 weight percent of a pressure sensitive adhesive composition as said matrix;

10 (b) from about 1 weight percent to about 95 weight percent of said gel dispersed in said pressure sensitive adhesive matrix, said gel comprising a hydrocolloid and a non-volatile hydrocolloid swelling agent having a ratio of weight fractions of hydrocolloid to swelling agent of from about 3:1 to about 1:99.

15 2. The composite according to Claim 1, wherein said pressure sensitive adhesive composition is hydrophobic and said hydrocolloid swelling agent is hydrophilic, wherein said gel has a shear modulus of less than about 6.2×10^6 dynes/cm², and wherein said gel in
20 said matrix has particle sizes of from about 1 to about 600 microns.

3. The composite according to Claim 1, wherein said pressure sensitive adhesive composition is an
25 acrylic copolymer comprising:

at least one monomer of an acrylic or methacrylic acid ester of an alkyl alcohol wherein said alkyl alcohol contains from 4 to 10 carbon atoms; and

30 at least one other monomer selected from the group consisting of acrylic acid, methacrylic acid, alkyl acrylates and methacrylates containing 1 to 3 carbon atoms in said alkyl group; acrylamide; methacrylamide; alkyl-substituted acrylamides containing 1 to 4 carbon atoms in said alkyl substituted group; diacetone
35 acrylamide; N-vinyl-2-pyrrolidone; and vinyl perfluoro-n-butyrate;

-83-

wherein said first monomer has a weight percent of from about 85 percent to about 98 percent and said other monomer has a weight percent of from about 2 percent to about 15 percent.

5

4. The composite according to Claim 1, wherein said pressure sensitive adhesive composition comprises at least one polymer selected from the group consisting of polyolefins, and polyvinyl ethers, silicone pressure sensitive adhesives and
10 polystyrene-polyisoprene-polystyrene block copolymers, a natural or synthetically derived rubber base adhesive composition.

15

5. The composite according to Claim 1, wherein said hydrocolloid comprises a poly (N-vinyl lactam), a polyvinyl alcohol, a polyoxyalkylene, a polyacrylamide, a polyacrylic acid, a polymer having nitrogen in the non-cyclic or cyclic monomeric backbone, a polystyrene sulfonate, a natural or synthetically modified
20 polysaccharide, an alginate, a xanthan gum, a guar gum, a natural or synthetically modified cellulose, or a linear or crosslinked polyhydroxyalkyl acrylate or methacrylate.

25

6. The composite according to Claim 2, wherein said non-volatile hydrocolloid swelling agent comprises a room temperature liquid polyol, a solid polyol blended with a room temperature liquid polyol, a monoanhydroalditol blended with a room temperature liquid
30 polyol, a monosaccharide, blended with a room temperature liquid polyol, a liquid ether alcohol, or a solid ether alcohol blended with a room temperature liquid polyol.

35

-84-

7. The composite according to Claim 1, wherein said pressure sensitive adhesive comprises isooctylacrylate/N-vinyl-2-pyrrolidone copolymer, said hydrocolloid comprises poly(N-vinyl pyrrolidone), and
5 said swelling agent comprises glycerol.

8. The composite according to Claim 1, further comprising a broad spectrum antimicrobial agent therein, wherein said antimicrobial agent comprises
10 parachlorometaxylenol, chlorhexidine and its salts, iodine, iodophors, poly (N-vinyl pyrrolidone) iodophors, silver oxide, silver and its salts, antibiotics or combinations thereof.

9. The composite according to Claim 1, wherein said pressure sensitive adhesive comprises from about 20 weight percent to about 95 weight percent of the composite and wherein said gel comprises from about 80 weight percent to about 5 weight percent of the
20 composite, and wherein said hydrocolloid and said non-volatile hydrocolloid swelling agent have a ratio of weight fractions of from about 1.5:1 to about 1:19.

10. The composite according to Claim 9,
25 wherein said pressure sensitive adhesive comprises from about 25 weight percent to about 90 weight percent of the composite, and wherein said gel comprises from about 75 weight percent to about 10 weight percent of the composite, and wherein said hydrocolloid and said
30 non-volatile hydrocolloid swelling agent have a ratio of weight fractions of from about 1:1.5 to about 1:19.

11. An article having a high moisture vapor transmission rate, comprising:
35 a gel-adhesive composite according to Claim 1 attached to a backing material.

12. An article according to Claim 11, further comprising a release liner and wherein said backing material comprises a film having moisture vapor transmission properties, a medical drape, a medical dressing, or a medical tape.

13. A method for preparing a composite of a gel dispersed in a pressure sensitive adhesive matrix having a high moisture vapor transmission rate, comprising:

(a) swelling a hydrocolloid with a non-volatile swelling agent to form swollen hydrocolloid gel particles;

(b) dispersing said gel particles into a hydrophobic solution comprising a pressure sensitive adhesive;

(c) coating said solution on a release liner; and

(d) drying said solution to form a continuous pressure sensitive adhesive matrix having said gel particles dispersed therethrough to form a gel-adhesive composite.

14. A method for preparing a composite of gel dispersed in a pressure sensitive adhesive matrix having a high moisture vapor transmission rate, comprising:

(a) swelling a hydrocolloid with a non-volatile swelling agent compatible with said hydrocolloid to form swollen hydrocolloid gel particles;

(b) dispersing said gel particles into a latex mixture comprising a pressure sensitive adhesive;

(c) coating said latex mixture on a release liner; and

(d) drying said latex mixture to form a continuous pressure sensitive adhesive matrix having said gel particles dispersed therethrough to form a gel-adhesive composite.

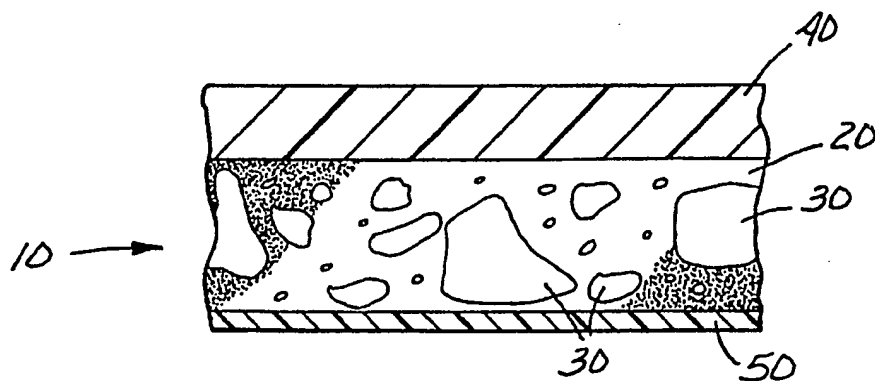
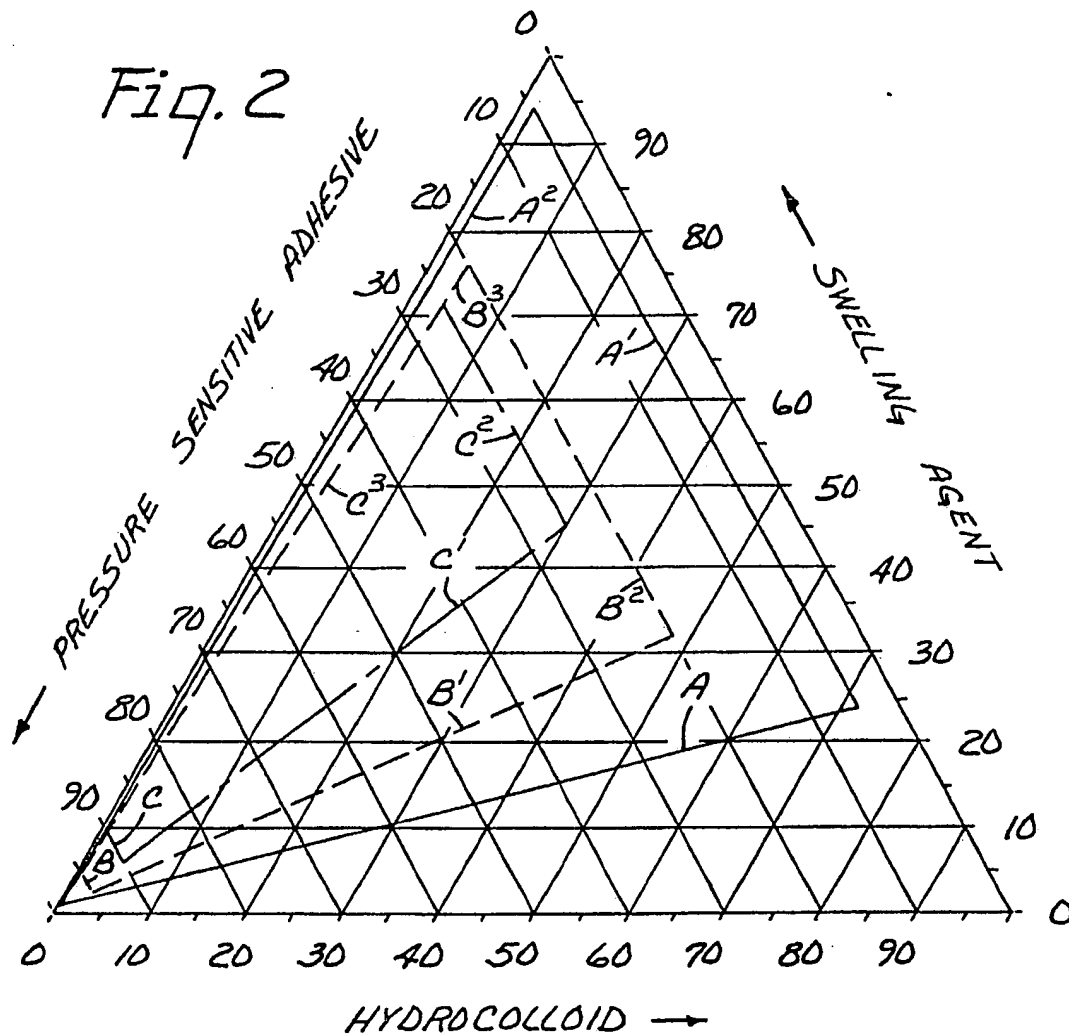


Fig. 1

INTERNATIONAL SEARCH REPORT

International Application No PCT/US 90/07412

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) *		
According to International Patent Classification (IPC) or to both National Classification and IPC IPC ⁵ : A 61 L 15/22, 15/58, 15/60, C 09 J 157/00		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
IPC ⁵	A 61 L, C 09 J	
Documentation Searched other than Minimum Documentation to the extent that such Documents are included in the Fields Searched *		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ⁸		
Category *	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X	GB, A, 2008000 (KAO SOAP) 31 May 1979 see claims; examples; page 1, line 59 - page 2, line 14; page 2, line 63 - page 3, line 3 --	1-6,9-12
X	EP, A, 0066887 (HOLLISTER) 15 December 1982 see claims; page 4, lines 1-31; page 6, lines 30-31 --	1-6,8-12
X	GB, A, 2046774 (ADVANCE TAPES) 19 November 1980 see claims; examples --	1-14
A	GB, A, 2061732 (KINGSDOWN MEDICAL CONSUL- TANTS) 20 May 1981 --	
A	EP, A, 0072251 (LECTEC CORPORATION) 16 February 1983 -----	
<div style="display: flex; justify-content: space-between;"> <div style="width: 45%;"> <p>* Special categories of cited documents: ¹⁰</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> </div> <div style="width: 45%;"> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p> </div> </div>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search 3rd May 1991	Date of Mailing of this International Search Report 20. 06. 91	
International Searching Authority EUROPEAN PATENT OFFICE	Signature of Authorized Officer miss T. MORTENSEN	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO.**

US 9007412
SA 44071

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 12/06/91
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB-A- 2008000	31-05-79	JP-C- 1010678	29-08-80
		JP-B- 54044688	27-12-79
		JP-A- 54070340	06-06-79
		DE-A- 2848977	17-05-79
		US-A- 4226915	07-10-80
EP-A- 0066887	15-12-82	US-A- 4534767	13-08-85
		US-A- 4578065	25-03-86
GB-A- 2046774	19-11-80	EP-A,B 0017401	15-10-80
		US-A- 4356819	02-11-82
GB-A- 2061732	20-05-81	AU-B- 537462	28-06-84
		AU-A- 6159780	09-04-81
		CA-A- 1151041	02-08-83
		EP-A,B 0026572	08-04-81
		JP-B- 1009864	20-02-89
		JP-C- 1524684	12-10-89
		JP-A- 56045667	25-04-81
		US-A- 4341207	27-07-82
EP-A- 0072251	16-02-83	AU-B- 553343	10-07-86
		AU-A- 7542481	24-03-83
		CA-A- 1206095	17-06-86
		US-A- 4675009	23-06-87

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ **BLACK BORDERS**
- ☐ **IMAGE CUT OFF AT TOP, BOTTOM OR SIDES**
- ☒ **FADED TEXT OR DRAWING**
- ☒ **BLURRED OR ILLEGIBLE TEXT OR DRAWING**
- ☐ **SKEWED/SLANTED IMAGES**
- ☐ **COLOR OR BLACK AND WHITE PHOTOGRAPHS**
- ☐ **GRAY SCALE DOCUMENTS**
- ☐ **LINES OR MARKS ON ORIGINAL DOCUMENT**
- ☐ **REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY**
- ☐ **OTHER:** _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.